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Effect of Coal Dewatering and Coal Use on the Water Quality of the East Poplar River, Saskatchewan: A Literature Review

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Management Perspective

The Poplar River basin in south-central Saskatchewan straddles the Canada-United States boundary above rich and exploitable lignite coal beds. Ground water in the basin has been found to contain naturally occurring radionuclides, as have the lignite coals. In general, mining has the potential to release radionuclides and metals to the aquatic and terrestrial ecosystems through mine dewatering, coal stockpile leaching, seepage from ash lagoons, and stack emissions.

The East Poplar River, which flows south from the Cookson Reservoir into the United States, is ultimately the recipient of all outflows from the reservoir and consequently is of international interest. Waters within the area under active development, including the Cookson Reservoir, may, in time, receive not just mine dewatering inflows but also seepage from ash lagoons. After five years of lagoon operation, contamination from ash lagoon seepage has not been documented. On-site spills present another potential source of radionuclides and metals. The upstream waters of Girard Creek and Cookson Reservoir receive dewatering water, local runoff, ground water, and direct precipitation.

This report is both a literature review and an assessment, and it places in perspective the potential environmental and human health risks associated with radionuclides and metals resulting from coal mining operations. In the opinion of both the Water Quality Branch and the National Hydrology Research Institute, the concentrations of radionuclides and metals in the receiving waters are sufficiently low as to pose no immediate danger to the environment or to humans. The report demonstrates, however, that there are many research questions and data gaps that need to be addressed.

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Abstract

This report is a literature review of the environmental behaviour and radiochemistry of uranium and thorium, and their radionuclide decay products, principally members of the U-238 decay series and He-4, in lignite and ground water from the Poplar River basin. A review of the trace element chemistry of ground water, lignite, and ash waste is also given. Emphasis is placed on trace elements that are potentially toxic in the environment, such as B, Be, F, Se, As, Cd, Th, and U. The chemical evolution of ground waters, especially dewatering ground water liberated during the mining process, is discussed in the context of the geological setting and hydrology of the basin. These studies are reviewed in relation to their relevance to coal mining activity and water quality in the Poplar River basin. An assessment is made of the bioavailability, toxicity, and potential ecological impacts of these contaminants in the East Poplar River and Girard Creek. As both of these streams flow into the Cookson Reservoir, the quality of water flowing from this reservoir into the Poplar and Missouri rivers is also considered. From this review, a number of information gaps and research needs are identified.

Résumé

Les auteurs ont effectué une étude bibliographique du comportement dans l'environnement et des propriétés radiochimiques de l'uranium, du thorium et de leurs descendants radioactifs, principalement les membres de la chaîne de désintégration de l'uranium 238 et l'hélium 4 se trouvant dans la lignite et les eaux souterraines du bassin de la rivière Poplar. Les caractéristiques chimiques des éléments en traces présents dans les eaux souterraines, la lignite et les cendres sont également passées en revue. Les auteurs se sont intéressés de façon particulière aux éléments en traces qui sont potentiellement toxiques dans l'environnement, comme le bore, le béryllium, le fer, le sélénium, l'arsenic, le cadmium, le thorium et l'uranium. L'évolution chimique des eaux souterraines, plus particulièrement des eaux d'égouttage libérées durant le procédé d'extraction, est examinée dans le contexte des caractéristiques géologiques et hydrologiques du bassin. Les études sont analysées en fonction de leur pertinence pour l'activité d'extraction du charbon et la qualité de l'eau du bassin de la Poplar. Une évaluation est présentée de la biodisponibilité, de la toxicité et des répercussions écologiques potentielles de ces éléments dans la rivière East Poplar et le ruisseau Girard. Comme les deux cours d'eau se déversent dans le réservoir Cookson, la qualité de l'eau à la sortie du réservoir dans les rivières Poplar et Missouri est également examinée. Les auteurs, à partir de cette étude, font ressortir un certain nombre de lacunes dans l'information disponible et indiquent des domaines où des recherches sont requises.

Radioactivity Units

The International System of Units (SI) has been used in this report. Basic SI radioactivity units are defined as follows.

Becquerel (Bq): A unit of measure of radioactivity which corresponds to one disintegration (transformation) per second (dps).

Gray (Gy): This unit is a measure of the biological effectiveness of radiation dose which represents the absorption of one joule of energy per kilogram of tissue.

Sievert (Sv): The radiation dose equivalent is expressed in sieverts and is obtained by multiplying the absorbed dose with a quality factor (Q), which is variable depending upon the nature of radiation. For example, the value of Q is 1 for beta particles and gamma rays, whereas for alpha particles it has a value of 20 (U.S. EPA, 1981). N represents any other modifying factors, and is usually assigned a value of unity.

EQUIVALENT UNITS

1 curie (Ci) is equal to 3.7×10^{10} dps, or Bq

1 rad is equal to 100 ergs/g, or 0.01 Gy

1 rem is equal to 100 ergs/g $\times$ Q $\times$ N, or 0.01 Sv

Effect of Coal Dewatering and Coal Use on the Water Quality of the East Poplar River, Saskatchewan: A Literature Review

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INTRODUCTION

Large volumes of ground water are released during lignite* mining in the Poplar River basin in south-central Saskatchewan, and concern has been expressed regarding the impact of this on the quality of surface water in the area and downstream in the United States. This report reviews aspects of the chemistry, bioavailability, toxicity, and potential ecological effects of soluble or particulate contaminants derived from uranium-rich coal seams and transported by means of dewatering ground waters. On the basis of this review, a number of important information gaps are identified concerning the radio- and trace-element chemistry of water and organisms in the Poplar River basin.

GEOGRAPHICAL BACKGROUND

Location and Drainage Patterns

The Poplar River basin is located in south-central Saskatchewan and northeastern Montana (Fig. 1). The basin is divided into three subbasins, the East Poplar, the Poplar, and the West Poplar basins (Fig. 2). (In the United States, they are designated as the East Fork, the Middle Fork, and the West Fork of the Poplar River. The Canadian designations are used exclusively in this report.) The total area of the Poplar River basin is 8620 km^2, 3150 km^2 of which are located in Saskatchewan. A large area of the basin in Montana (about 2230 km^2) lies within the Fort Peck Indian Reservation (Fig. 1).

Although the main part of the Poplar River valley ranges in width from about 3 to 6 km, tributary streams within the basin are significantly narrower. In Saskatchewan, both the East Poplar River and Girard Creek flow into the Cookson Reservoir. The Poplar River and its tributaries are shallow, low-gradient prairie streams that flow in a south-southeasterly direction. The Poplar River is an important tributary of the Missouri River, which it joins near Poplar, Montana.

Girard Creek is of considerable importance to the hydrology of the Poplar River basin because it passes through the Coronach area, where lignite is being strip-mined for the Saskatchewan Power Corporation. In the process of this operation, significant volumes of dewatering ground water enter Girard Creek and ultimately the Cookson Reservoir on the East Poplar River, approximately 5 km north of the Canada-United States border. The storage capacity of the Cookson Reservoir is 41 166 dam^3. The reservoir was constructed by the Saskatchewan Power Corporation to provide a supply of cooling water for the Poplar River generating station (International Poplar River Water Quality Study, 1979a).

Fife Lake, an internal drainage area within the Poplar River basin in Saskatchewan, does not contribute to the flow of the Poplar River system during years when runoff is normal. However, overflow from Fife Lake into the Poplar River occurs at intervals of about 10 years (International Joint Commission, 1981).

Landforms

The topography of the basin is gently rolling with low relief. A number of different terrain types are recognized: *(a)* widespread rolling uplands, e.g., the Cypress Hills, Wood Mountain, the Flaxville Plateaux, and the Missouri Coteau, which are underlain by sand, silt, clay, sandstone, siltstone, and lignite; *(b)* river valleys and adjacent uplands covered with glacial or fluvio-glacial deposits; *(c)* gravel terraces; *(d)* river valley alluvial deposits; and (e) lake sediments. Further details of the geomorphology of this area of southern Saskatchewan are given in Parizek (1964).

* Lignite is a coal of relatively recent origin, intermediate between peat and subbituminous coal. In this report, lignite and coal have sometimes been used interchangeably.

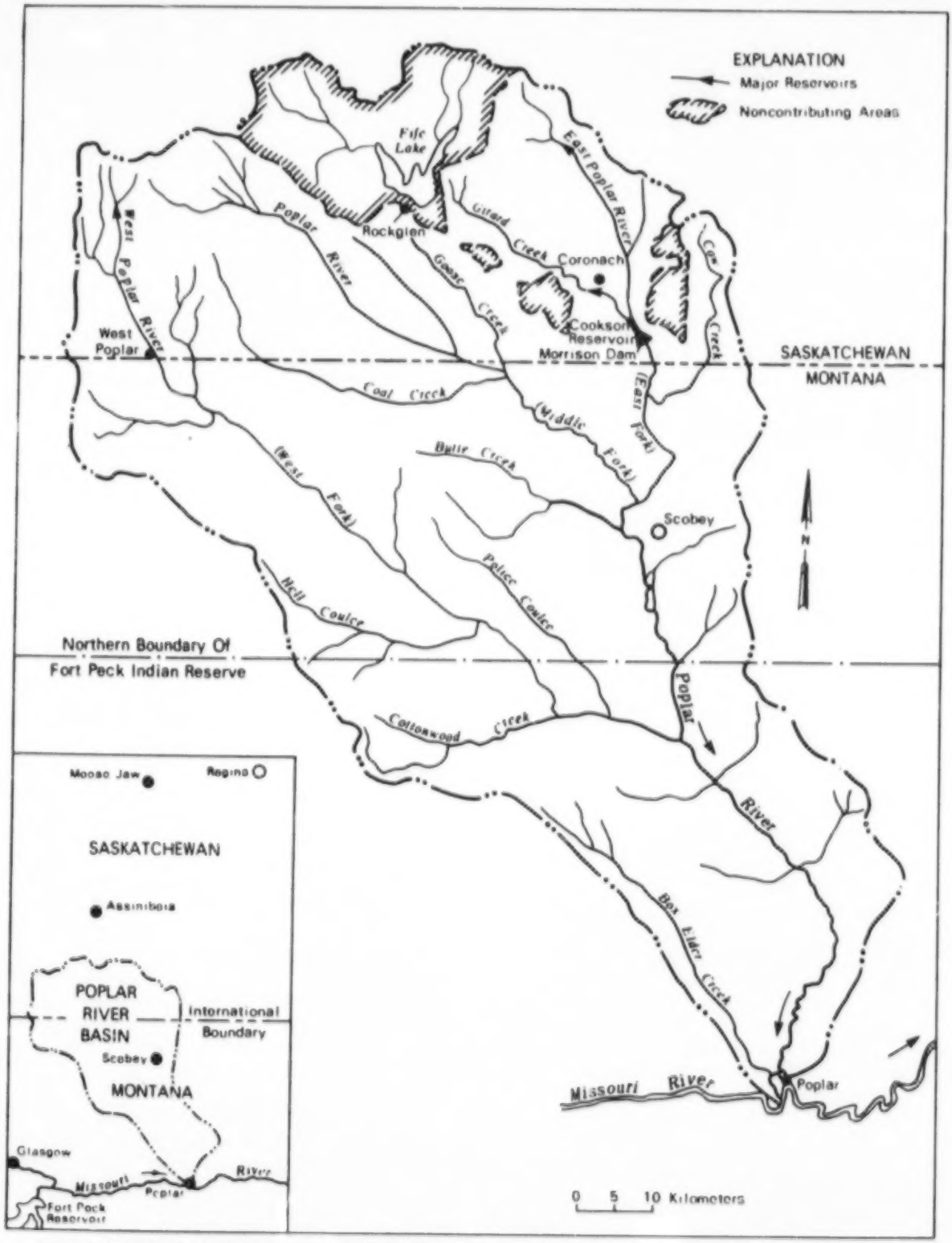

Figure 1. Location and drainage patterns of the Poplar River basin. (From International Poplar River Water Quality Study, 1979a, Figure 1.1.)

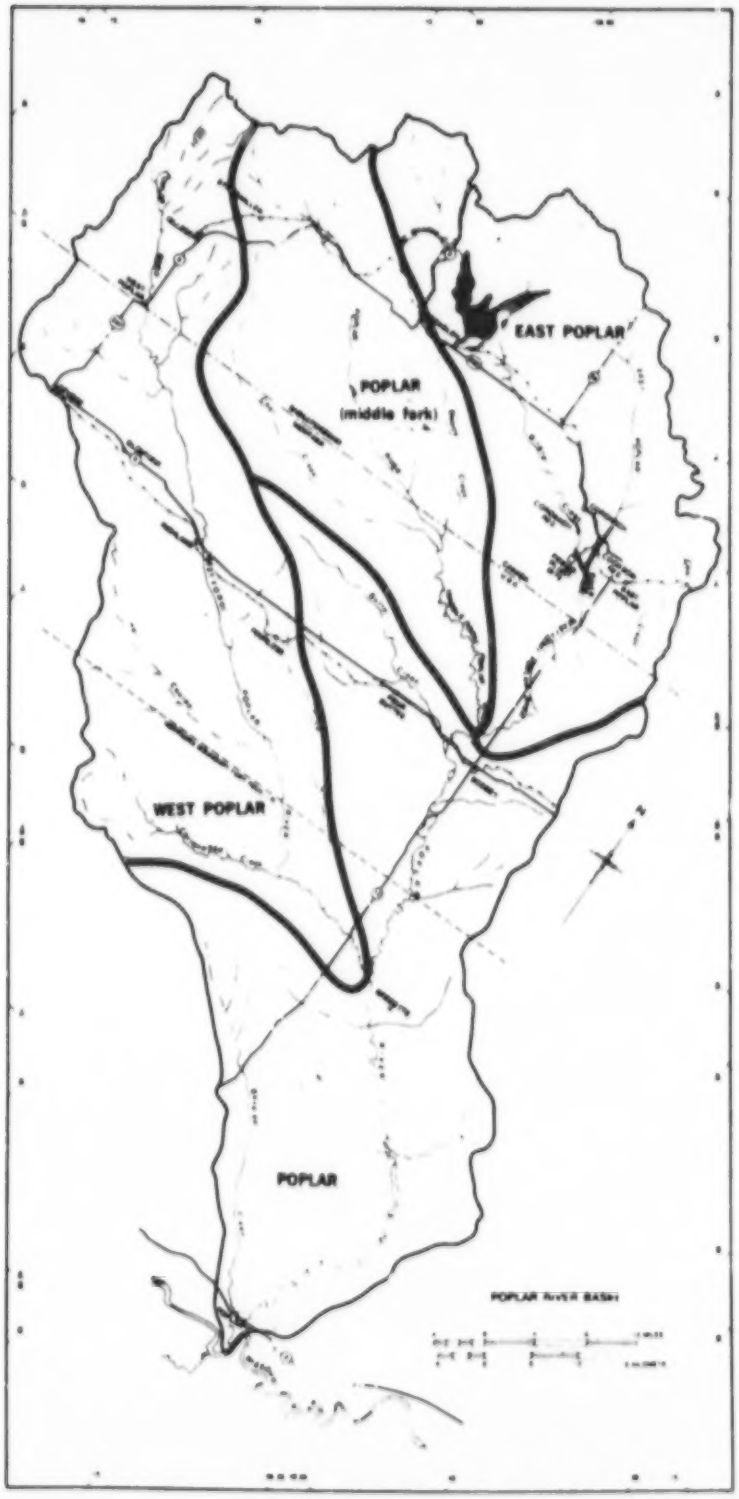

Figure 2. Subbasins in the Poplar River basin. (From International Poplar River Water Quality Study, 1979a, Figure 3.1.)

Soil Types

Soils in the Poplar River basin are developed principally on till and glacial lake clay horizons, although local development on glacial outwash sands and gravels or bedrock exposures are also observed (Parizek, 1964). Soil types include sandy and clay loam on the upland areas and alluvial soils in stream valleys. Brown chernozemic soils overlain by light brown to greyish brown surface horizons with low organic matter occur at the Coronach mine site. However, local depressions and sloughs contain gleysolic soils derived from glacial till and bedrock.

Climate

The climate of the basin is characterized by cold, dry winters, warm, wet springs, and warm to hot, dry summers. The mean January temperature is $-13.5°C$, and the mean temperature in July is 19°C. The average annual precipitation for the basin ranges from 300 to 400 mm. The area is semiarid, surface water is scarce, and peak flows occur during the period of spring runoff mostly as a result of snowmelt. Flow during this period accounts for about 75% of the total annual discharge from the basin. More complete details of climatic conditions in the basin are given in Canadian Climate Normals (1982).

GEOLOGICAL BACKGROUND

The Williston Basin

The Poplar River basin occurs within the upper part of the Phanerozoic Williston basin (Fig. 3). The latter forms an irregularly shaped intracratonic depression on the western edge of the Canadian Shield in Manitoba, Saskatchewan, North and South Dakota, and Montana (Gerhard et al., 1982; Kent, 1987) and is one of the largest marine sedimentary sequences in North America. The Williston basin has extensive fossil fuel and mineral resources, principally oil and natural gas (Christopher et al., 1973), as well as lignite and potash.

Sediments in the Williston basin lie unconformably on Precambrian basement gneisses and granitoids and reach a total thickness of about 5500 m. During the Late Cambrian and Ordovician, the basin was part of a broad shelf. The first sediments to be deposited were clastic sandstones and shales, as well as carbonates. During the Middle Ordovician to Late Devonian, carbonates and evaporites were deposited in a shallow epicontinental sea. At the start of Mississippian, reducing conditions prevailed. Open marine depositional environments were reestablished and massive carbonates deposited during the latter part of this period. Evaporites were deposited during the Permian-Triassic. In the Jurassic and Cretaceous, shales and sandstones interbedded with minor carbonate units were deposited. At this time, uplift, erosion, and volcanism occurred in the Rocky Mountains supplying detritus to the basin (Gerhard et al., 1982). Terrestrial rocks (shaly sandstones, lignite, and layers of volcanic ash) were deposited during the Tertiary and Quaternary. The presence of Tertiary sediments in the present centre of the basin indicates that the basin persisted into the Tertiary. Regional basin structure is also reflected in the distribution of the Paleocene Ravenscrag (Fort Union) formation (Gallup and Hamilton, 1954). The deposition of Paleocene coal measures represents the major event in the geological evolution of the Williston basin (Guliov, 1972). The boundaries of this coal basin are shown in Figure 4. Detailed regional stratigraphic correlations for units in the Williston basin are shown in Figure 5.

Figure 3. Location of the Williston basin. (Gerhard et al., 1982, Figure 1; reprinted with permission.)

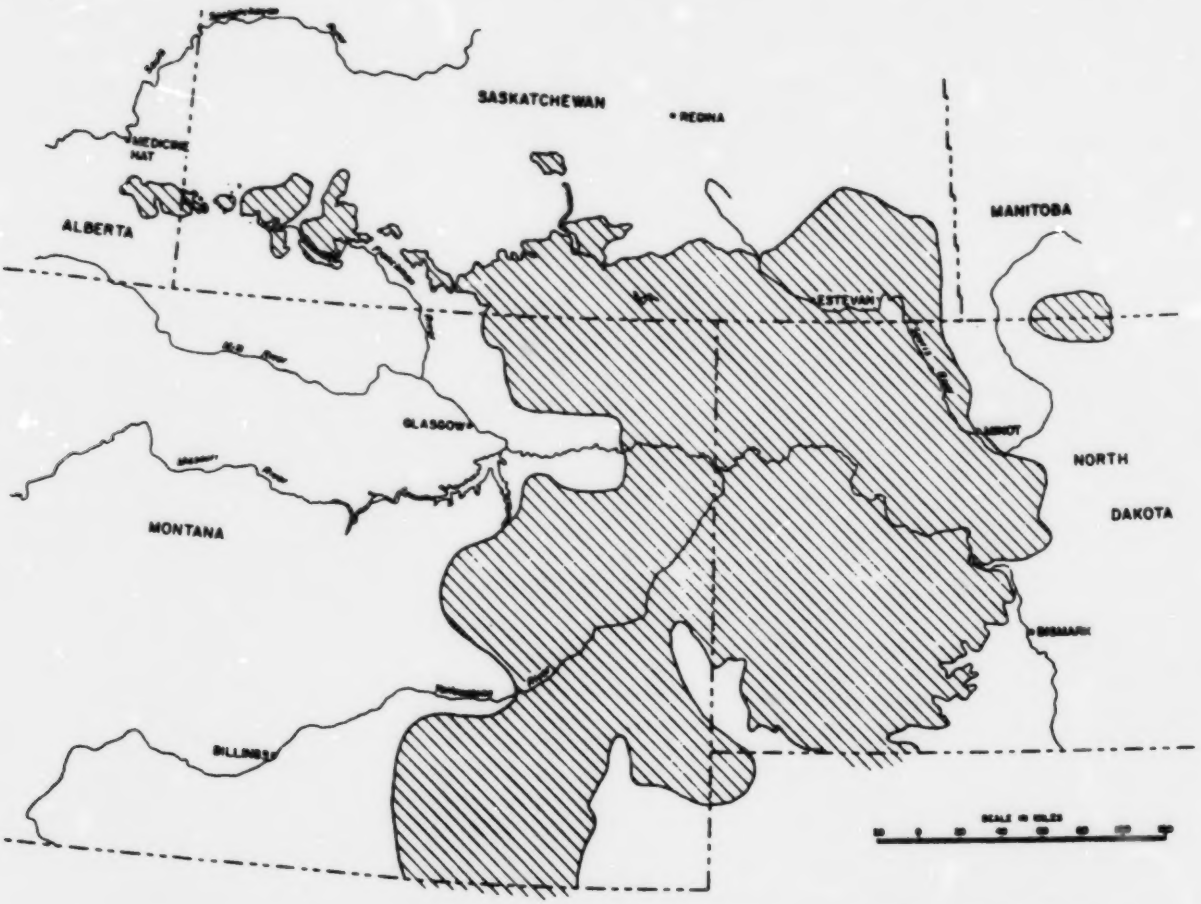

Figure 4. Boundaries of the Paleocene coal basin within the Williston basin. (Guliov, 1972, Figure 3; reprinted with permission.)

Geology of the Coronach Area

A detailed geological map of the upper Poplar River basin in Saskatchewan and Montana is given in Figure 6. Relationships of geological rock units that crop out in the vicinity of the Coronach mine are also shown in Figure 6. The stratigraphy of this area is summarized in Figure 7. Units in Figure 6 are present within a depth of 365 m at the Coronach mine. Formations and units in ascending order are (1) the Ravenscrag formation and its correlative, the Fort Union formation in Montana; (2) the Wood Mountain formation (Flaxville formation, Montana); (3) the Empress group (Wiota gravels, Montana); (4) glacial deposits; (5) alluvial deposits (consisting of valley-fill alluvium); and (6) lake deposits.

The Cretaceous Bearpaw formation, a thick sequence of marine silts and clays, is less permeable than the overlying Frenchman, Ravenscrag, and Wood Mountain formations and is considered to act as an aquitard to ground-water flow in the overlying sediments (International Poplar River Water Quality Study, 1979a).

The Upper Cretaceous Frenchman formation is composed of deltaic sands and silts, which form sheet-like bodies that have great lateral continuity over the entire Coronach area. However, the Frenchman formation, like the Bearpaw formation, is not exposed at the surface in the general vicinity of the East Poplar River basin.

The Ravenscrag formation consists of interbedded sand, silt, clay, and lignite in narrow lenticular bodies. The Paleocene coal basin, as shown in Figure 4, contains a number of lignite horizons, which are used locally as marker beds. One of these, the Hart coal seam, is exploited in the Coronach area for the Saskatchewan Power Corporation.

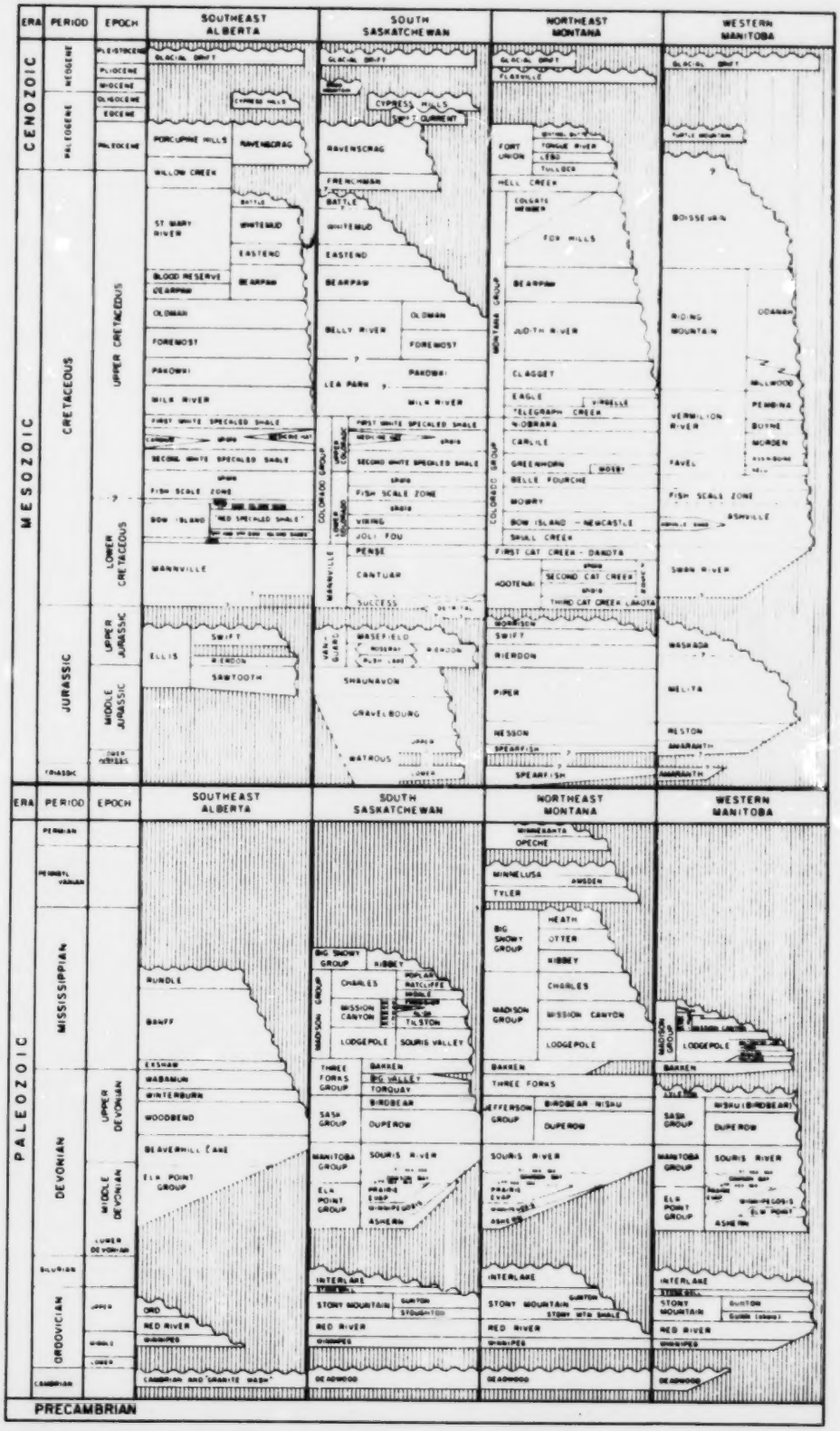

Figure 5. Stratigraphy of the Williston basin. (Christopher et al., 1973, Figure 5; reprinted with permission.)

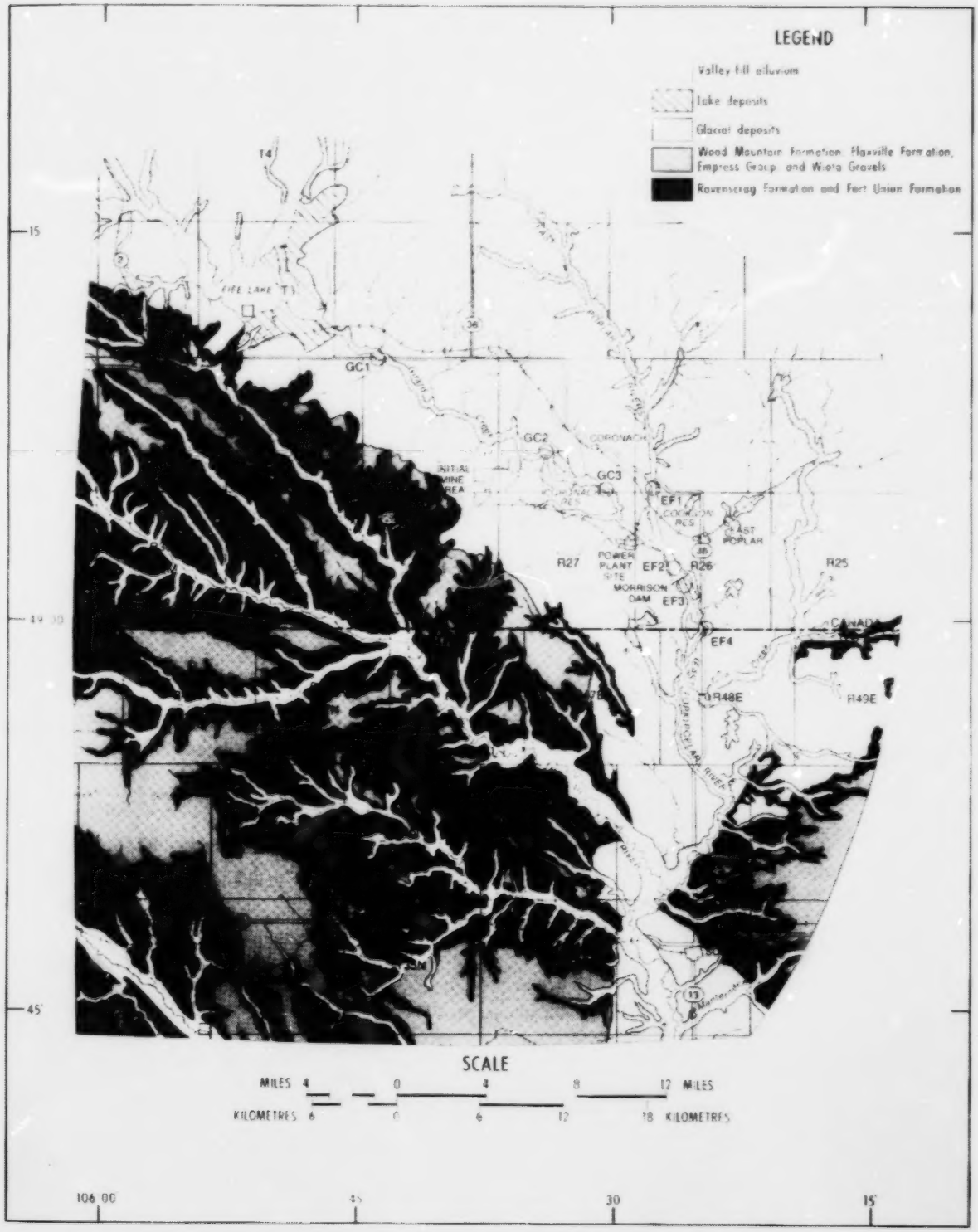

Figure 6. Geological map of the upper Poplar River basin. (From International Poplar River Water Quality Study, 1979a, Figure 2.1.)

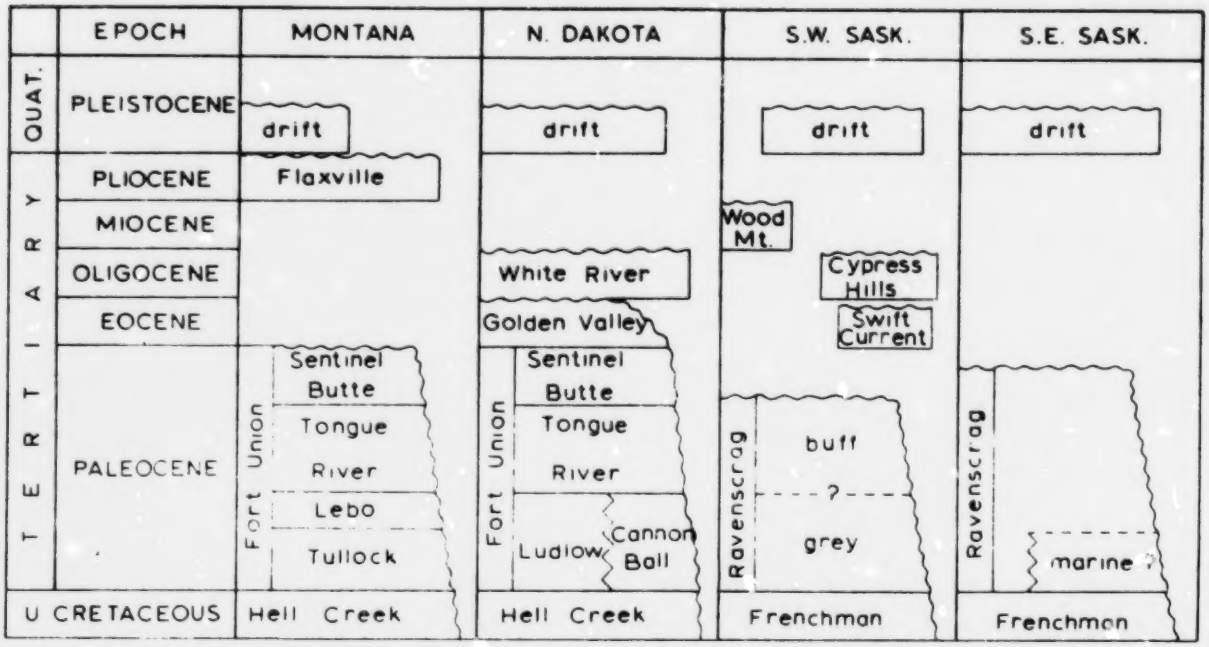

Figure 7. Stratigraphic correlations between different Tertiary and Quaternary units. (Guliov, 1972, Figure 2; reprinted with permission.)

Units of the Miocene age Wood Mountain formation consisting of sand and gravel with minor silt and clay beds overlie the Ravenscrag formation and are exposed in upland areas. Surficial deposits, as well as glacial, alluvial, and lake sediment deposits make up the Empress group. The Empress group was deposited prior to the first Pleistocene glaciation of the area (Whitaker and Vonhof, 1978). The glacial till deposits and the alluvial and lake deposits consist of unconsolidated material derived from adjacent upland areas. Lake sediments are concentrated around Fife Lake and other minor inland drainage depressions.

MINING ACTIVITY AND DEWATERING

Three major coal fields have been developed in the Ravenscrag formation at Estevan, at Coronach, and in the Cypress Hills-Shaunavon area. There appears to be a general decrease in thermal quality of the lignite from east to west across the basin (Guliov, 1972). The exploited seam is thickest and of the highest quality at Coronach near the centre of the Poplar River basin, where it averages between 2.4 and 3.7 m, although locally the seam reaches 5.5 m in thickness. Lignite, present in the Hart coal seam in the Coronach area, is a low sulphur, high ash, very high moisture-content coal with moderate thermal capability. Coal reserves are estimated to last for approximately 35 years (International Joint Commission, 1981).

The Hart coal seam is currently being exploited to fuel a thermal power station at Coronach. During these mining operations, it has been found necessary to remove excess water from within and from the strata that overlie the lignite horizon, as these units are important aquifers for ground-water flow in the area. In the Coronach area, 14 locations are being monitored and pumped at a monthly rate of about 680 dam^3. In 1983, 8348 dam^3 of water were removed from these wells (Poplar River Bilateral Monitoring Committee, 1984). Discharge from this source mainly occurred into Girard Creek, with subordinate flow from one well into the west end of Cookson Reservoir and from another well into a tributary of Goose Creek. This water flux, combined with sump drainage and water diversion at the mine site is reported to have had a significant effect on ground-water and surface-water flow (International Joint Commission, 1981).

HYDROGEOLOGY OF THE UPPER POPLAR RIVER BASIN

The results of hydrological studies in the upper Poplar River basin are summarized in Whitaker and Vonhof (1978), International Poplar

River Water Quality Study (1979b), International Joint Commission (1981), and Poplar River Bilateral Monitoring Committee (1984). Shallow ground-water aquifer systems in the area appear to be dominantly recharged by local precipitation. Flow occurs from recharge areas of relatively high local relief (where the water table is elevated) to discharge areas of lower relative relief. Ground-water flow, therefore, appears to be largely controlled both by the topology of the water table and by the physical characteristics, namely, hydraulic conductivity, transmissivity, and storage coefficient. The principal areas of natural recharge from precipitation are considered by the International Poplar River Water Quality Study (1979b) to occur in upland exposures of the Wood Mountain and Flaxville formations and in valley-fill alluvial deposits. Natural discharge occurs as springs and as flow from valley-fill aquifers into stream systems. A schematic diagram of ground-water flow within aquifers in the different formations that overlie the Bearpaw formation is shown in Figure 8. These aquifers are listed in Table 1 and their hydrological properties are given in Table 2. The Bearpaw formation appears to behave as an aquitard because it is located at the base of a region of high hydraulic conductivity (Freeze, 1969). During periods of low surficial flow in the Poplar River, Girard Creek, and their tributaries, natural discharge from ground-water aquifers increases. This results in surface waters with significantly higher contents of total dissolved solids.

HYDROGEOCHEMISTRY OF SURFACE AND GROUND WATER IN THE UPPER POPLAR RIVER BASIN

Although geochemical studies have been undertaken on surface and ground waters since the inception of coal mining activity in the vicinity of Coronach (see, for example, Whitaker and Vonhof, 1978; International Poplar River Water Quality Study, 1979b; International Joint Commission, 1981; Poplar River Bilateral Monitoring Committee, 1984; and Inland Waters Directorate, 1982), no integrated investigation of the effect of aquifer geochemistry on surface water chemistry in the area has been undertaken. This is in spite of indications from reconnaissance ground-water studies that such relationships may be extremely important (Fig. 9).

Surface Waters

It is clear from the previously mentioned hydrogeochemical studies that chemical variations in surface waters are strongly influenced by seasonal effects. The magnitude of these seasonal variations is shown in Table 3. Surface waters are markedly alkaline with median pH values ranging from 7.6 to 9.1. Significantly, the waters are most

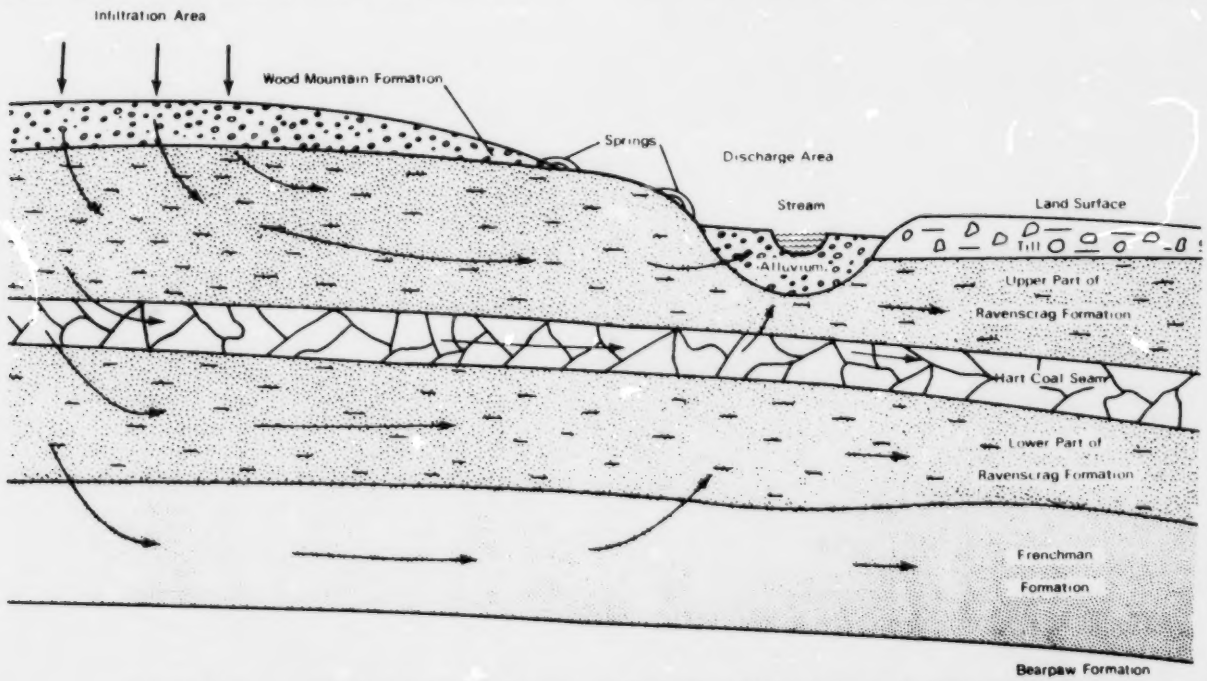

Figure 8. Ground-water flow lines. (From International Poplar River Water Quality Study, 1979a, Figure 5.2.)

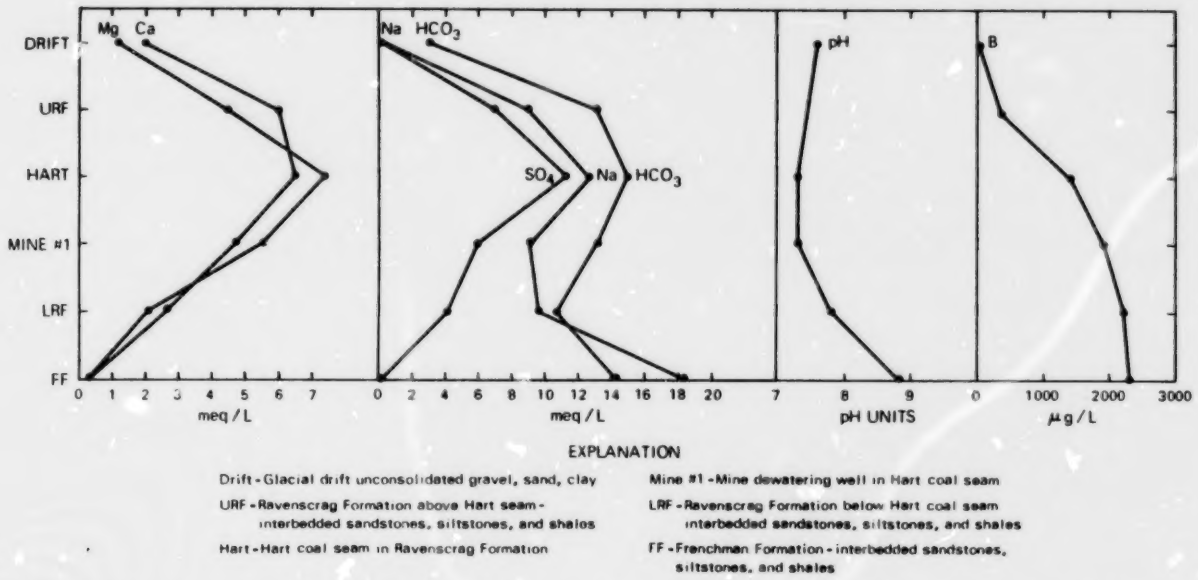
DRIFT
URF
HART
MINE #1
LRF
FF
Mg Ca
Na HCO3
SO4 Na HCO3
pH
B
0 1 2 3 4 5 6 7
meq/L
0 2 4 6 8 10 12 14 16 18 20
meq/L
7 8 9
pH UNITS
0 1000 2000 3000
µg/L
EXPLANATION
Drift - Glacial drift unconsolidated gravel, sand, clay
URF - Ravenscrag Formation above Hart seam - interbedded sandstones, siltstones, and shales
Hart - Hart coal seam in Ravenscrag Formation
Mine #1 - Mine dewatering well in Hart coal seam
LRF - Ravenscrag Formation below Hart coal seam interbedded sandstones, siltstones, and shales
FF - Frenchman Formation - interbedded sandstones, siltstones, and shales

Figure 9. Variations in concentration of selected elements in different aquifers in the Poplar River basin. (From International Poplar River Water Quality Study, 1979b, Figure 9.)

Table 1. Generalized Aquifer Layers of the Upper Poplar River Basin, Saskatchewan and Montana

Layer	Canada	United States
5	Valley-fill alluvium, glacial deposits, and Wood Mountain Formation	Valley-fill alluvium, glacial deposits, and Flaxville Formation
4	Upper Ravenscrag Formation	Upper Fort Union Formation
3	Hart coal seam	Lignite, horizon D (Collier, 1925)
2	Lower Ravenscrag Formation	Lower Fort Union Formation and upper Hell Creek Formation
1	Frenchman Formation	Lower Hell Creek Formation and Fox Hills Sandstone

(From International Poplar River Water Quality Study, 1979b, Table 4.)

alkaline during the summer — a feature ascribed to the alkaline nature of soils in the region. There is an excellent correlation between pH increase and the elevated levels of total dissolved solids (TDS) during the summer. The high TDS values are, therefore, probably related to an increased ground-water flux (Table 3). Concentrations of bicarbonate and sulphate also show similar seasonal increases. Waters in the Cookson Reservoir exhibit similar high values of pH, TDS, SO_4^{2-}, and HCO_3^-, but do not reveal any significant seasonal variations (Inland Waters Directorate, 1982). This presumably reflects the combined effect of seasonal runoff and ground-water discharge.

Ground Water

Ground-water chemistry is strongly dependent on *(a)* the concentration of anions and pH of water in the recharge area, *(b)* the nature of mineral dissolution reactions, *(c)* chemical equilibrium between the water and the aquifer, *(d)* the residence-time of water within the aquifer, *(e)* water temperature, and *(f)* the nature of reactions taking place as waters permeate the soil profile (Freeze and Cherry, 1979; Drever, 1982). Although the chemistry of ground water in the Poplar River basin is highly variable (International Poplar River Water Quality Study, 1979b), analyses do not exhibit the same seasonal variability in ground-water chemistry as shown by the surface waters. The waters are generally slightly alkaline, are enriched in $NaHCO_3$, and have relatively high contents of total dissolved solids (100–1200 mg/L). They show variation with respect to *(a)* Ca^{2+}, Na^+, and Mg^{2+}, *(b)* BO_3^{3-}, HCO_3^-, and SO_4^{2-}, and *(c)* pH between different aquifers. These variations are illustrated in Figure 9. Water in the Ravenscrag formation above the Hart coal seam has been reported to contain high concentrations of dissolved U (190 µg/L)

Table 2. Estimated Hydrologic Characteristics of Generalized Aquifer Layers of Upper Poplar River Basin, Saskatchewan and Montana

Layer		Saturated thickness (m)	Mean transmissivity (m^2/d)	Mean horizontal hydraulic conductivity (m/d)	Mean vertical hydraulic conductivity (m/d)	Ratio of horizontal hydraulic conductivity to vertical hydraulic conductivity	Storage coefficient or specific yield
	Valley-fill alluvium----	0–60	4.7×10^{2}	4.4×10^{1}	4.4×10^{0}	10:1	2.0×10^{-1}
5	Glacial deposits----	0–25	3.7×10^{-3}	3.5×10^{-4}	3.5×10^{-5}	10:1	5.0×10^{-2}
	Wood Mountain Formation and Flaxville Formation----	0–14	9.5×10^{1}	8.9×10^{0}	8.9×10^{-1}	10:1	2.0×10^{-1}
4		0–130	3.7×10^{1}	9.8×10^{-1}	9.8×10^{-4}	1,000:1	1.0×10^{-3}
3		0–5	5.0×10^{1}	2.0×10^{1}	4.0×10^{0}	5:1	4.0×10^{-3}
2		50	3.7×10^{1}	7.4×10^{-1}	1.9×10^{-4}	4,000:1	1.0×10^{-3}
1		60	7.4×10^{1}	1.2×10^{0}	3.0×10^{-4}	4,000:1	2.8×10^{-4}

(From International Poplar River Water Quality Study, 1979b, Table 5.)

Table 3. Seasonal Variation in Selected Water Quality Parameters for the East Poplar River at International Boundary and for Mine Discharge Well Number 1

	Surface water			Ground water
Date	3/18/76	7/17/75	12/19/75	5/9/78
Discharge (m^3/s)	1.5	1.2	0.008	N/A
pH	7.9	9.1	7.6	7.3
Dissolved Solids (mg/L)	97	1,480	1,180	1,070
Calcium (mg/L)	12	28	81	95
Magnesium (mg/L)	4.8	63	51	67
Sodium (mg/L)	12	390	280	210
Bicarbonate (mg/L)	73	717	929	800
Sulfate (mg/L)	20	500	270	290
Silica (mg/L)	3.3	0.9	21	15
Boron (μg/L)	120	2,100	2,300	1,900

(From International Poplar River Water Quality Study, 1979b, Table 7.)

and Se (63 μg/L) (International Poplar River Water Quality Study, 1979b). These values are significant because the mobility of U in ground waters is enhanced by oxidation (Hodge et al., 1973; Langmuir, 1978). The lignite at Coronach is dewatered before exposure to surface oxidizing conditions during mining. The high U content of water released from the lignite indicates that this water is oxygenated and is not buffered by the reducing environment of the coal seam.

Boron concentrations up to 3.0 mg/L have been reported from waters associated with the Hart coal seam and the lower Frenchman formation. Relatively high B levels have also been reported in the Cookson Reservoir (Inland Waters Directorate, 1982) and in other surface waters during the summer and fall/winter (Table 3). There appears to be a positive correlation between enhanced B concentrations and high levels of Mo and F in some of the ground waters.

Comparative hydrogeochemical data for ground water from shallow lignite aquifers in North Dakota are given in Table 4. Ground water of similar quality and variability to these and similar waters from the Poplar River basin have been reported throughout the plains area of western North America (Rahn, 1976; Van Voast, 1974; Van Voast et al., 1977, 1978; Williams et al., 1978).

A general geochemical model for the chemical evolution of the ground water in the Poplar River basin is presented in the International Poplar River Water Quality Study (1979b). A similar model has also been proposed by Groenewold (1979) and Groenewold et al. (1981) for waters associated with coal-bearing sediments in western North Dakota. A number of evolutionary stages explain the chemical evolution of the majority of the ground waters in the area.

Stage 1: Recharge to Water Table

The saturated zone between the land surface and water table is extremely important in the chemical evolution of the ground waters (Moran et al., 1978; Groenewold et al., 1979). During this stage of evolution, oxygenated water reacts with soil and porous rocks causing dissolution of carbonates and pyrite and results in the formation of waters with a low pH (6.5–7.5) containing high amounts of Ca^{2+}, Mg^{2+}, Fe^{3+}, SO_4^{2-}, and HCO_3^-. At this stage, the water is considered to be saturated with respect to carbonate. These geochemical processes are illustrated in Figure 10. Acidity in this zone is considered to be the result of CO_2 production during biochemical decay of organic matter and also to oxidation of pyrite. The pH is effectively buffered by dissolution of the carbonate phases. Alternating wet and dry cycles in the upper 2–3 m of the profile result in the concentration of soluble salts such as gypsum. During periods of anomalously high precipitation, ground-water recharge occurs. This is considered to result in CO_2 production and dissolution of gypsum generating significant concentrations of SO_4^{2-}. Calcite and dolomite dissolution, at the same time, elevates the HCO_3^- content of the ground water.

Stage 2: Movement through Aquifer

Processes taking place during movement through the aquifer to the area of discharge include sulphate reduction and cation exchange of Ca, Mg, and Sr for Na on Na-montmorillonitic clays (Groenewold et al., 1981). Carbonate saturation is maintained because of elevated pH values (8.5–9.0) facilitating the exchange reactions. Waters of this type typically have low contents of Ca (6 mg/L), Mg (2.5 mg/L), and Sr (0.15 mg/L). These waters occur near the surface in areas of natural discharge. However, they are also typical of waters in the deeper Frenchman formation aquifer. The generation of similar high Na-HCO_3^- waters at depth in aquifers associated with lignite seams in North Dakota is interpreted to be largely the result of sulphate reduction (Groenewold et al., 1981). Common reactions that take place within ground waters are shown in Table 5.

This model for the evolution of Na^+-, Ca^{2+}-SO_4^{2-}, and HCO_3^- type ground water in the Poplar River basin and in similar environments in North Dakota illustrates the effect of recharge geology on ground-water chemistry. When recharge occurs through clay and silt-rich sediments, Na^+ liberated from montmorillonitic clays and SO_4^{2-} produced by pyrite oxidation and dissolution of gypsum become the dominant ions in the ground water. However, when recharge occurs through sediments that are poor in Na-montmorillonitic clays and pyrite, ground waters will be of a Ca^{2+}-HCO_3^- and Ca^{2+}-SO_4^{2-} type. Where recharge occurs through sand and silty sand, Ca-HCO_3^- is dominant. The only significant chemical activity taking place below the water table is SO_4^{2-} reduction and cation exchange reactions. The high degree of variability in ground-water chemistry of waters associated with fractured coal aquifers

Table 4. Summary of Chemical Analyses of Ground Water from Shallow (Less than 75 m) Lignite Aquifers at the Five North Dakota Study Sites

	Field Temp. °C	Field pH	Field Cond. μS	TDS	Ca	Mg	Na	K	HCO_3	Cl	SO_4
						mg/L					
Falkirk Site — Hagel Lignite Bed											
$\bar{x}$	7.9	7.3	1603.0	1169.0	122.9	66.4	174.5	8.8	575.5	16.0	447.2
s	0.7	0.5	1332.2	1210.3	104.9	53.1	228.5	5.4	185.4	18.3	680.2
n	10	7	10	10	10	10	10	10	10	10	10
high	9.0	7.75	5000	4310	400	204.8	620	20.2	932.1	46.9	2264
low	7	6.46	630	195	36.2	20.4	9.5	4.4	378	0.5	20.6
Indian Head Site — Beulah-Zap Lignite Bed											
$\bar{x}$	—	7.6	3213.4	2617.6	51.7	30.9	742.8	27.6	1099.6	20.0	937.4
s	—	0.2	1803.9	1564.4	25.9	11.7	414.4	7.3	616.0	12.0	516.0
n	—	4	5	5	5	5	5	5	5	5	5
high	—	7.83	5587	4390	75.0	44	1107	35.5	1663	37.7	1608
low	—	7.28	1497	938	19.4	12.8	278	18.5	415	8.2	409
Beulah-Hazen Site — Various Lignite Beds											
$\bar{x}$	7.5	7.48	2700.0	1480.1	39.1	24.6	415.5	10.3	818.7	14.5	427.8
s	4.2	1.01	1874.3	853.3	37.2	19.9	337.6	7.3	465.6	12.4	321.7
n	9	5	6	12	12	12	12	12	12	12	12
high	12	8.69	6250	3380	87	54.1	1039	31.4	1779	39.8	1211
low	1	6.07	1100	482	3.0	2.4	99	4.5	221	4.3	123
Center Site — Kinneman Creek Lignite Bed											
$\bar{x}$	10.4	6.7	1655.6	1229.3	84.3	51.9	249.7	18.8	651.1	8.1	372.2
s	2.8	4.6	437.1	333.3	47.0	20.3	122.7	11.3	208.7	8.0	137.5
n	9	9	9	9	9	9	9	9	9	9	9
high	16.0	7.5	2200	1631.0	165.0	94.4	441.0	48.0	1021.1	21.0	642.7
low	6.5	6.0	975	838.0	29.0	29.0	115.0	11.4	334.3	0.5	232.6
Dunn Center Site — Various Lignite Beds											
$\bar{x}$	9.3	7.06	3000	1602.5	113.0	56.1	388.0	11.1	665.3	16.5	821.1
s	2.2	—	—	831.3	108.8	39.3	226.9	7.3	375.9	18.7	591.5
n	4	1	1	4	7	7	7	7	7	6	7
high	12	—	—	2256	334	103	700	23	1405	38	1760
low	7.0	—	—	413	8.0	1.0	71	2.4	350	2.7	70

(From Groenewold et al., 1981, Table 1.)

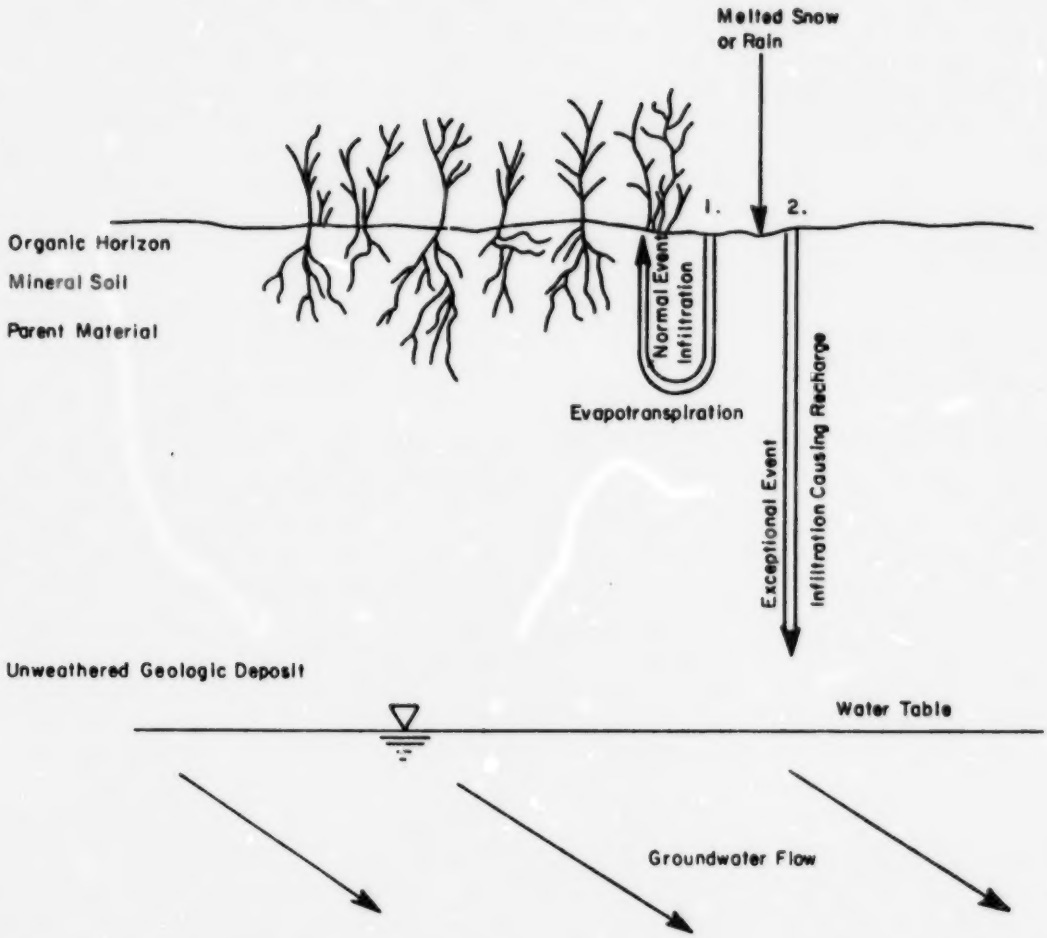

Figure 10. Types of chemical processes and salt movement mechanisms in coal-bearing units similar to those in the Poplar River basin. (Moran et al., 1978, Figure 4.7; reprinted with permission.)

in the western United States is considered by Groenewold et al. (1981) to reflect mixing between components derived from localized sites in the overlying sediments.

TRACE ELEMENT GEOCHEMISTRY OF COAL

To develop a picture of the chemical evolution of dewatering waters from the Poplar River coal development, it is necessary to evaluate the trace element geochemistry of coal. In a pioneering study of trace elements in coal, Goldschmidt (1937) suggested three concentration mechanisms: (1) concentration in plants, (2) concentration by residual enrichment in soil, and (3) concentration by selective reactions between element-enriched ground waters and carbonaceous materials. A number of comprehensive studies of the trace element chemistry of coals in the United States have been undertaken (see, for example, Gluskoter et al., 1977).

The principal conclusions of Gluskoter et al. (1977) concerning the trace element geochemistry of coal are as follows:

(a) Elements that exhibit the largest ranges in concentration occur in distinct mineral phases.

(b) Only B, Cl, Se, and As appear to be enriched relative to their crustal abundances.

(c) Coals from the same area commonly exhibit wide ranges in elemental abundances.

Table 5. Chemical Representation of Major Processes in the Chemical Evolution of Soil, Water, and Ground Water in Shallow Tertiary and Cretaceous Deposits in Western North Dakota (Groenewold et al., 1979)

1/

CO_2 production in organic horizons of the soil

$CH_2O + O_2 \rightarrow CO_2 + H_2O$

2/

Oxidation of pyrite

$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 16H^+ + 8SO_4^{2-}$

3/

Dissolution of calcite and dolomite

$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$

$CaMg(CO_3)_2 + 2H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^-$

4/

Precipitation and dissolution of gypsum

$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O$

$CaSO_4 \cdot 2H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$

5/

Cation exchange

$Ca^{2+} + 2Na$ (adsorbed) $\rightleftharpoons 2Na^+ + Ca$ (adsorbed)

$Mg^{2+} + 2Na$ (adsorbed) $\rightleftharpoons 2Na^+ + Mg$ (adsorbed)

(From Groenewold et al., 1981, Table 2.)

Average trace element concentrations in a variety of different coal types and of major and minor elements in United States coals are given in Tables 6 and 7, respectively. A regional survey of the trace element geochemistry of coal from deposits in five Canadian provinces was undertaken by Landheer et al. (1982). Compositional ranges from coal from a number of Canadian localities, including Poplar River, are presented in Table 8. Selected trace element data for coals from the Shaunavon area in Saskatchewan are given in Table 9. A limited amount of geochemical data for coal from Estevan is also given in Cameron and Birmingham (1971).

Coal from the Poplar River area is enriched in B, F, Mn, Ga, Y, Zr, Nb, Ba, Th, and U relative to coal from the other localities. Other trace elements in the Poplar River lignite, including La, Ce, Sm, Eu, Mo, Sr, V, and Sc, are present in concentrations similar to those reported from the other Canadian localities (Landheer et al., 1982). Relative to crustal elemental abundance levels (Table 8), the Poplar River lignite is enriched in B, S, As, Se, Mo, and U. There is significant discrepancy between B levels quoted for two Poplar River lignites by Landheer et al. (1982) and the mean value for coals from the same area given by Evans et al. (1985), namely, 1858 and 1415 mg/kg and 265 ± 18 mg/kg, respectively (Table 8).

The high boron levels exhibited by some coals have been interpreted to reflect paleosalinity in the coal depositional environment (Couch, 1971). However, Drever (1982) has suggested that anomalous concentrations of trace metals in coal develop as a result of the formation of chelate-type complexes during the passage of water through organic material.

Uranium in Coal

Studies by Szalay (1964), Muto et al. (1968), and Doi et al. (1975) have shown that adsorption of the uranyl ion onto organic materials from ground water plays an important role in uranium concentration processes. As a result, uranium is commonly associated with carbonaceous materials such as lignite (Moore, 1954). Laboratory studies by Moore (1954) have indicated that low rank coals (lignites) are among the most effective types of carbonaceous materials for extracting U from solution. Similar studies carried out by Cameron and Leclair (1975) showed the importance of solution pH in controlling the adsorption of U.

Uraniferous lignites of economic grade have been reported from the Williston basin by Denson et al. (1959), Denson and Gill (1965), and Cameron and Birmingham (1970). Data presented in Cameron and Birmingham (1970) indicate that the uranium content of southern Saskatchewan lignite is highly variable. Uranium values for coal in the Estevan area range up to 17 mg/kg. In the Cypress Hills, the coals are significantly more radioactive, with U contents up to 700 mg/kg. These values are between 1 and 2 orders of magnitude greater than U concentrations reported for western Canadian coals by Landheer et al. (1982). Coal in the Coronach area exhibits a highly variable distribution of uranium. Concentrations reported by N. Worsley (Feb. 22, 1985, pers. comm.) indicate variations between 3.5 and 12.4 mg/kg over the thickness of the Hart coal seam. The average concentration of U in the Hart coal seam at Coronach is 2.6–5.0 mg/kg (Worsley).

Both Th and U show significant increases in concentration in ash at the Poplar River generating station over levels reported for lignite fuel (Table 8). Data presented by Evans et al. (1985) indicate Th contents in bottom ash, ESP ash, and emitted ash

Table 6. Average Trace-elements Contents for Coals from Various Regions of the U.S.[a]

Element	SWI[b]	EI[c]	NGP[d]	APP[e]
B	33	96	116	25
Be	1.1	2.5	1.5	2.5
Co	4.6	3.8	2.7	5.1
Cr	13	20	7	13
Cu	11	11	15	15
Ga	2.0	4.1	5.5	4.9
Ge	5.9	13	1.6	5.8
La	6.5	5.1	9.5	9.4
Mo	3.1	4.3	1.7	3.5
Ni	14	15	7.2	14
Sn	1.3	1.5	0.9	0.4
Ti	250	450	591	350
V	18	35	16	21
Y	7.4	7.7	13	14
Zn	108	44	59	7.6

[a] ppm.
[b] SWI = Forty-eight coals from Western and Southwestern Interior Region.
[c] EI = Eastern Interior Region, 53 coals.
[d] NGP = Northern Great Plains Region, 51 samples.
[e] APP = Seventy-three coals from Appalachian region.

Source: Zubovic et al., 1961, 1964, 1966, 1967.

(From Wewerka et al., 1976, Table IV-II.)

of 24.9, 25.7, and 33.3 mg/kg, respectively. Uranium concentrations in the same populations of ash are 13.8, 15.2, and 26.5 mg/kg. By contrast, ash from the Cypress Hills area contains over 3500 mg/kg U (Cameron and Birmingham, 1970). In a study of radioactivity in Canadian coals and ashes, Dearborn (1985) reported concentration factors for U and Th of between 2 and 10 times in fly ash relative to coal. The increased U and Th levels in ash is the resultant concentration due to combustion of volatile materials.

Towse (1957) and Denson and Gill (1965) both suggested that the U in the North Dakota lignites was leached from overlying volcanic rocks in ground waters and adsorbed by carbonaceous material. The source of the U in the Saskatchewan coals has yet to be evaluated.

URANIUM GEOCHEMISTRY OF GROUND WATER

Uranium occurs in four valence states: U^{3+}, U^{4+}, U^{5+}, and U^{6+}. In natural waters, uranium is commonly present in the hexavalent state, forming the stable divalent uranyl ion, UO_2^{2+}. A number of factors influence the behaviour of uranium in ground water (Langmuir, 1978). These include

1. the content and leachability of U in source rocks, aquifer lithologies, and recharge area soils
2. the proximity of the aquifer to uranium-bearing lithologies
3. the extent to which ground water is hydraulically isolated from compositionally different freshwater supplies
4. the influence of evapotranspiration
5. the pH and redox potential state of the water (Hostetler and Garrels, 1962)
6. the concentrations of ionic species, such as carbonate, phosphate, vanadate, fluoride, sulphate, silicate, calcium, and potassium, which can form uranium complexes or result in the crystallization of uranium minerals
7. the presence of sorptive phases, such as organic material.

These factors produce constant or negligible effects on U levels in deeper aquifers or large rivers

Table 7. Range of Trace Elements in U.S. Coals[a]

Major Elements[b]		Minor Elements	
Element	Range (%)	Element	Range (ppm)
Na	0 - 0.20	Be	0 - 31
Mg	0.1 - 0.25	B	1.2 - 356
Al	0.43 - 3.04	F	10 - 295
Si	0.58 - 6.09	P	5 - 1430
Cl	0 - 0.56	Sc	10 - 100
K	0.02 - 0.43	V	0 - 1281
Ca	0.05 - 2.67	Cr	0 - 610
Ti	0.002 - 0.32	Mn	6 - 181
Fe	0.32 - 4.32	Co	0 - 43
Zn[c]	0 - 0.56	Ni	0.4 - 104
		Cu	1.8 - 185
		Ga	0 - 61
		Ge	0 - 819
		As	0.5 - 106
		Se	0.4 - 8
		Br	4 - 52
		Y	< 0.1 - 59
		Zr	8 - 133
		Mo	0 - 73
		Cd	0.1 - 65
		Sn	0 - 51
		Sb	0.2 - 9
		La	0 - 98
		Hg	0.01 - 1.6
		Pb	4 - 218
		U	<10 - 1000

[a] References used were Ruch et al. (1974), Abernethy and Gibson (1962), Zubovic et al. (1961-1967), Sun et al. (1971) and Magee et al. (1973). (Data by Deul and Annell in these references have been omitted.)

[b] Elements present in 0.2% in coals.

[c] Zinc is not normally considered a major element in coals.

(From Wewerka et al., 1976, Table IV-V.)

(Langmuir, 1978). However, they can result in significant variations in the U levels in smaller streams (Rose, 1977). Although adsorption plays an extremely important role in the behaviour of uranium in natural waters at low temperatures, precipitation induced by reduction processes may also be an effective means of influencing the amount of uranium in such waters (Masuda and Yamamoto, 1971).

Uranium transport generally occurs in oxidizing surface and ground waters as the uranyl ion (UO_2^{2+}, UO_2^{+}). In natural waters, uranium commonly forms complexes with carbonate, hydroxide, phosphate, fluoride, and sulphate (Langmuir, 1978). These complexes increase the solubility of uranium-bearing phases as well as the mobility of uranium in surface and ground waters. The nature of complexing is strongly influenced by the availability of appropriate complexing ligands in the water and also by pH.

The nature of these complexing processes with respect to uranium has been thermochemically investigated by Langmuir (1978). Uranyl carbonate complexes are important species at low temperatures (25°C) in ground waters with a partial pressure of CO_2 of 10^{-2} atm. However, their stability is strongly temperature-dependent and at 100°C and CO_2 fugacity of 10^{-2}, or less, uranyl carbonate complexes are less important than hydroxyl complexes over the entire pH range. Uranyl phosphate complexes appear to be extremely stable in waters containing PO_4 concentrations of 0.1 mg/kg over a pH range from 4 to >10. Fluoride complexing appears to be most important at pH values of less than 4 in reducing ground waters containing typical fluoride concentrations.

Element	Poplar River, Sask.	Nanticoke, Ont.	Battle River, Alta.	Lingan, N.S.	Crustal Average
H (%)	2.55 ± 0.18			4.45 ± 0.10	
Be (mg/kg)	0.38 ± 0.04	0.79 ± 0.22	0.43 ± 0.19	1.1 ± 0.3	2.8
B (mg/kg)	265 ± 18	61 ± 1	193 ± 32	12.1 ± 7.7	10
C (%)	32.5 ± 3.0	72.1 ± 1.4	50.9 ± 6.6	67.1 ± 1.1	0.002
F (mg/kg)	89 ± 6	66 ± 2	47 ± 34	70 ± 11	625
Na (%)	0.14 ± 0.06	0.055 ± 0.0047	0.22 ± 0.26	0.066 ± 0.014	2.8
Mg (%)	0.48 ± 0.095	0.063 ± 0.010	0.20 ± 0.07	0.088 ± 0.012	2.1
Al (%)	2.52 ± 0.30	1.32 ± 0.06	1.76 ± 0.72	1.82 ± 0.35	8.1
Si (%)	3.43 ± 0.77	1.86 ± 0.087	2.48 ± 0.32	2.63 ± 0.49	27.7
P (%)	0.030 ± 0.007	0.020 ± 0.003	0.038 ± 0.005	0.080 ± 0.016	0.11
S (%)	0.61 ± 0.049	1.61 ± 0.04	0.57 ± 0.06	2.35 ± 0.03	0.026
Cl (mg/kg)	133 ± 13	1785 ± 88	41 ± 37	2598 ± 590	130
K (%)	0.27 ± 0.06	0.085 ± 0.008	0.12 ± 0.03	0.33 ± 0.06	2.6
Ca (%)	2.20 ± 0.07	0.48 ± 0.03	1.15 ± 0.05	0.15 ± 0.015	3.6
Sc (mg/kg)	2.32 ± 0.37	2.81 ± 0.17	1.75 ± 0.28	3.47 ± 0.27	22
Ti (%)	0.097 ± 0.02	0.062 ± 0.003	0.034 ± 0.0035	0.075 ± 0.011	0.44
V (mg/kg)	28 ± 5	22.2 ± 1.7	4.95 ± 1.09	32.1 ± 3.3	135
Cr (mg/kg)	11.4 ± 2.7	12.5 ± 1.2	35.5 ± 25.5	22.7 ± 4.6	100
Mn (mg/kg)	185 ± 21	28.3 ± 3.4	51.6 ± 23.1	121 ± 30	950
Fe (%)	0.69 ± 0.17	0.86 ± 0.095	0.68 ± 0.16	3.47 ± 0.38	5
Co (mg/kg)	1.77 ± 0.33	3.2 ± 0.3	0.99 ± 0.09	7.8 ± 0.6	25
Ni (mg/kg)	7.1 ± 2.0	10.9 ± 1.4	9.85 ± 2.04	21.1 ± 1.2	75
Cu (mg/kg)	14.4 ± 1.3	10.1 ± 0.8	7.7 ± 1.4	21.2 ± 1.6	55
Zn (mg/kg)	11.1 ± 3.1	14.1 ± 2.0	9.2 ± 5.2	53 ± 12	70
Ga (mg/kg)	6.8 ± 0.9	4.4 ± 0.4	5.0 ± 2.7	5.9 ± 0.8	15
As (mg/kg)	10.4 ± 2.7	4.9 ± 0.7	4.8 ± 9.8	94 ± 14	1.8
Se (mg/kg)	2.5 ± 0.2	2.0 ± 0.14	1.4 ± 0.2	3.3 ± 0.2	0.05
Br (mg/kg)	1.31 ± 0.14	11.6 ± 1.0	1.6 ± 0.4	40.8 ± 7.5	2.5
Rb (mg/kg)	10.78 ± 3.11	6.1 ± 0.7	3.0 ± 0.8	20.3 ± 5.4	90
Sr (mg/kg)	315 ± 33	132 ± 2.9	331 ± 37	56 ± 10	375
Y (mg/kg)	8.9 ± 1.0	7.9 ± 0.8	5.8 ± 1.1	6.9 ± 0.3	33
Zr (mg/kg)	73 ± 6	37 ± 3	47 ± 9	22.7 ± 1.3	165
Nb (mg/kg)	5.2 ± 0.4	2.8 ± 0.6	2.7 ± 0.8	2.4 ± 0.3	20
Mo (mg/kg)	5.5 ± 0.5	1.7 ± 0.4	1.6 ± 0.2	5.6 ± 1.0	1.5
Ag (mg/kg)	0.073 ± 0.011	<.02	0.079 ± 0.026	0.68 ± 0.068	0.07
Cd (mg/kg)	0.080 ± 0.027	0.047 ± 0.005	0.21 ± 0.05	0.19 ± 0.07	0.2
Sb (mg/kg)	0.70 ± 0.09	0.62 ± 0.11	0.46 ± 0.14	2.10 ± 0.40	0.2
Cs (mg/kg)	1.04 ± 0.28	0.46 ± 0.064	0.29 ± 0.08	1.83 ± 0.23	3
Ba (mg/kg)	698 ± 306	245 ± 31	683 ± 68	91 ± 11	425
La (mg/kg)	11.2 ± 0.8	7.5 ± 0.5	7.2 ± 2.0	11.8 ± 0.6	30
Ce (mg/kg)	21.5 ± 5.8	14.6 ± 1.6	15.3 ± 4.7	27.7 ± 0.6	60
Sm (mg/kg)	1.4 ± 0.1	1.4 ± 0.16	1.2 ± 0.4	1.77 ± 0.07	6
Eu (mg/kg)	0.31 ± 0.036	0.29 ± 0.03	0.13 ± 0.025	0.41 ± 0.018	1.2
Hg (mg/kg)	0.122 ± 0.019	0.13 ± 0.03	0.090 ± 0.028	0.13 ± 0.098	0.08
Tl (mg/kg)	<0.05	<.5	<0.05	1.56 ± 0.25	0.5
Pb (mg/kg)	13.1 ± 1.8	3.78 ± 0.78	7.7 ± 3.2	39.4 ± 9.4	13
Th (mg/kg)	5.8 ± 0.7	2.31 ± 0.11	4.1 ± 2.1	3.02 ± 0.24	7.2
U (mg/kg)	3.2 ± 0.2	1.18 ± 0.17	1.3 ± 0.3	2.39 ± 0.64	1.8

(Modified from Evans et al., 1985, Table 6.2.)

At sulphate concentrations of about 100 mg/kg, uranyl sulphate is an important species at pH values in excess of 7.

Uranium precipitates from aqueous solution when it undergoes reduction to UO_2 (Langmuir, 1978). This is thermodynamically possible at Eh values between +80 and −50 mV under near neutral to slightly alkaline conditions (pH 7–8). However, in reducing environments, uranium commonly occurs as the tetravalent uranous ion (U^{4+}) and precipitation of uranium occurs as coffinite $USiO_4$ or as other species whose compositions are influenced by available anions in solution (Morin, 1983).

According to Osmond and Cowart (1976), dissolved U concentrations in most ground waters range from about 0.001 μg/L (ppb) to 1 mg/L (ppm). There is a general correlation between lower concentrations (<1 μg/kg) in aquifers that are reducing. The highest levels of dissolved uranium occurring on a regional scale in the United States are found in the western high plains, where the average concentration is about 2.2 mg/kg (Scott and Barker, 1962). This U is considered to be derived by weathering of volcanic ash in Tertiary sandstone aquifers. Arendt et al. (1980) and Spalding and Druliner (1981) have shown that a positive correlation commonly exists between U and the amount of TDS. The positive correlation of U and TDS probably reflects the higher degree of aqueous complexing discussed above. However, increased levels that are unrelated to TDS can also occur (Spalding and Druliner, 1981). These are considered to result from changes in oxidation state within the aquifer, which cause a release of U adsorbed onto organic material and Fe-Mn-Ti oxyhydroxides (Langmuir, 1978).

Uranium and radon concentrations in ground waters from southern Saskatchewan range from subdetection levels to between 240 μg/L and 4100 pCi/L (152 Bq/L), respectively (Dyck et al., 1976). In this study, a correlation was shown to exist between well depth and uranium and radon levels; the lower levels were present in deeper wells in the same aquifer formation. A strong positive correlation was also observed between alkalinity and uranium content in the ground waters. The following model was suggested to explain these observations: *(a)* leaching of U from surface rocks and lignite; *(b)* solution transport into the aquifer; *(c)* radon-loss by decay (and diffusion?); and *(d)* uranium-loss by precipitation or lateral dilution.

Table 9. Selected Trace Element Analyses of Coal from Shaunavon

Element	S-73	S-76	S-77
As (mg/kg)	2.1	3.7	15
Pb (mg/kg)	15	24	11
Se (mg/kg)	1.3	1.6	0.8
Cd (mg/kg)	0.5	0.4	0.4
Be (mg/kg)	1.9	2.6	2.0
V (mg/kg)	16	23	20
U (mg/kg)	2.2	3.0	5.2

(Data from Dr. B. Kybett, University of Regina.)

However, a more plausible explanation of the patterns described above is that the deeper wells are more reducing and thus favour precipitation of uranium, whereas the higher alkalinity in the upper wells enhances uranium solubility as a result of U-carbonate aqueous complexing.

Reviews of U levels in a variety of water types have been made by Fix (1956), Koczy (1963), Rogers and Adams (1970), Cothern and Lappenbusch (1983), and Dearborn (1985). A summary of these data for different terrestrial environments is presented in Table 10. The background level of uranium in streams from the United States was shown by Fix (1956) to be 0.1 μg/L. However, waters from uraniferous areas contained higher values, e.g., 1–10 μg/L in surface waters and 1–120 μg/L in ground waters. In uranium mine waters, the typical range is 15–400 μg/L (Fix, 1956). Uranium concentrations in river waters, reported by Cothern and Lappenbusch (1983) range from 0.02 μg/L in the St. Lawrence River to 1.6 μg/L in the Ganges-Bramaputtra rivers.

Under the National Radionuclides Monitoring Program, radionuclide concentration data for selected Canadian surface waters were recently reported by Baweja et al. (1987). Between the monitoring years 1981 to 1984, the mean U concentration in the East Poplar River was 2.84 ± 0.76 μg/L. This value is about twice as high as the mean U value for Canadian surface waters given in this report, namely, 1.35 μg/L. However, it is about half of that quoted by Dearborn (1985) for western United States river waters (Table 10).

RADIONUCLIDE BEHAVIOUR AND RADIOCHEMISTRY OF COAL AND GROUND WATER

The products of three radioactive decay series are potentially present in coal and associated

ground waters (Koester and Zieger, 1978), namely, *(a)* the uranium series, which originates as a result of the decay of U-238; *(b)* the thorium series, derived from the decay of Th-232; and *(c)* the actinium series, originating from U-235 decay.

The first member of each decay series has a relatively long half-life, i.e., 4500 Ma for U-238, 14 000 Ma for Th-232, and 700 Ma for U-235. Other members of the series have shorter half-lives. These decay schemes are shown in Figure 11. A number of the daughter radionuclides are extremely important with respect to environmental radiotoxicity. Isotopes important from an environmental point of view include thorium-230, radium-226, radon-222, lead-210, polonium-210, radium-228, thorium-228, and radon-220 (Koester and Zieger, 1978). One of the most significant of these nuclides is radon-222, a short-lived ($t_{½}$ = 3.8 days) mobile gas produced by alpha-decay of radium-226, which has a half-life of 1622 years. The daughter products of Rn-222 decay shown in Figure 11 provide a source of widespread and measurable radioactivity at the surface of the earth (Koester and Zieger, 1978).

Radionuclides in the environment are rarely in equilibrium (the parent-to-daughter nuclide ratio is not constant) because of varying mobilities exhibited by parent and daughter isotopes. For example, U-238 is leached from soil, rocks, and coal significantly more readily than the daughter isotopes Th-230, Ra-226, Pb-210, and Pb-206 (Patzer, 1976) because uranium forms soluble ionic complexes (Langmuir, 1978; Sheppard, 1980). Radium-226 is relatively immobile except under conditions of low pH. Lead-210 is also relatively immobile and is partitioned into sulphides and sulphates (Dyck, 1974). Precipitation of these phases depends on total lead concentrations (of which Pb-210 is a minor component). If total Pb in solution remains constant, Pb-210 can vary by orders of magnitude without causing the precipitation of a Pb-bearing phase. However, if total Pb increases in concentration, precipitation begins and Pb-210 levels can be changed substantially due to isotopic partitioning and isotopic exchange (S.R. Moran, 1986, Saskatchewan Environment, pers. comm.). Excess Pb-210 commonly found in lake and river sediments might be accounted for by atmospheric processes by means of the decay of Rn-222 into Pb-210 as a daughter product of Rn-222 decay (Dearborn, 1985).

Table 10. Uranium Concentrations in Various Natural Waters

Water Type or Location	Uranium Concentration (mg/L)
World Average	0.001
	0.006
Natural Surface Water	0.001
	0.002
Mineralized Water	0.050
	0.460
	0.600
Ocean Water	0.000 36 to 0.059
	0.001 to 0.005
	0.003
	0.003
	0.003
	0.0033
	0.0033
Freshwater	0.0001
	0.0006
	0.001
	0.001 to 0.010
United States River Water	0.0005
Western United States River Water	0.005
India	0.000 01 to 0.007
Black and Mediterranean Seas	0.002
Amazon River	0.000 04

(From Dearborn, 1985, Table 2.)

Radioactivity of coal is caused by the naturally occurring nuclides U-238, Th-232, their daughter isotopes, and K-40. Uranium occurs with organic material, whereas thorium and potassium partition into inorganic minerals (Breger et al., 1955). In a comprehensive study of the radionuclide contents of United States coals, Beck et al. (1979) showed that U and Th concentrations were greater in lignite than in coals of higher rank (Fig. 12). A compilation of radionuclide concentrations and activities for Canadian coals by Dearborn (1985) is given in Table 11 and is also shown in Figures 12 and 13. It is clear that the Canadian lignites have significantly higher U-238 concentrations than lignites compiled in the United States study.

Radionuclide concentrations in Poplar River lignite are presented in Table 12. Although the concentrations are higher than in other Canadian coals, they are nevertheless within the range reported for coal by Beck (1980) (cited in Evans et al., 1985). According to Evans, the Poplar River coals show evidence of significant disequilibrium in the U-238 decay series. For example, Th-230 has twice the activity of its U-238 parent, and the activity of Ra-226 is only about 40% of the Th-230.

Radionuclides liberated to the air during coal combustion broadly reflect the original concentration of Th and U in the fuel (Dearborn, 1985). If radionuclide levels are enhanced over background

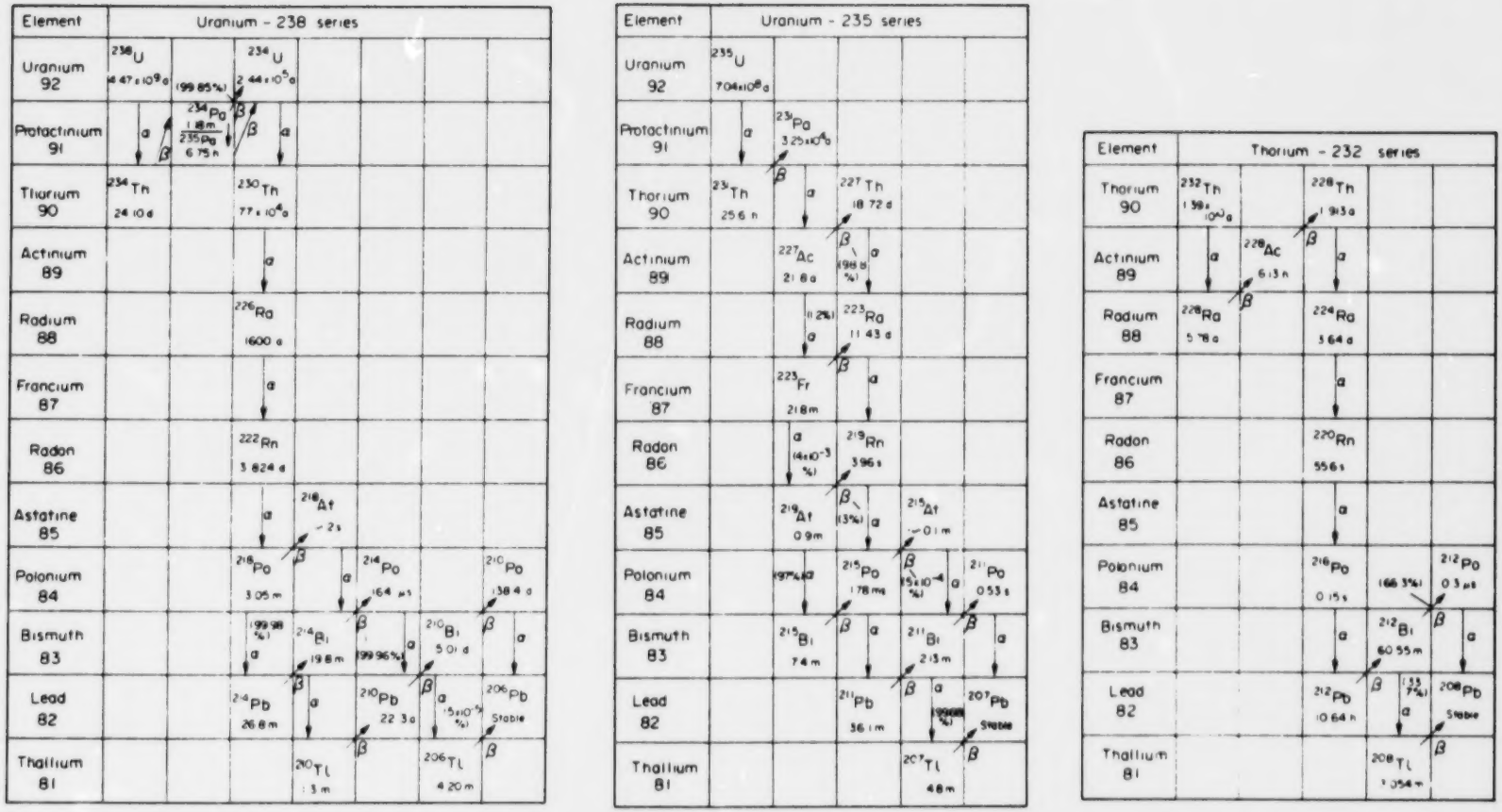

Figure 11. Decay series for U-238, U-235, and Th-232. (Reprinted with permission from P. Henderson, Inorganic Geochemistry, 1982, Pergamon Press, Oxford; Figures 9.1, 9.2, and 9.3.)

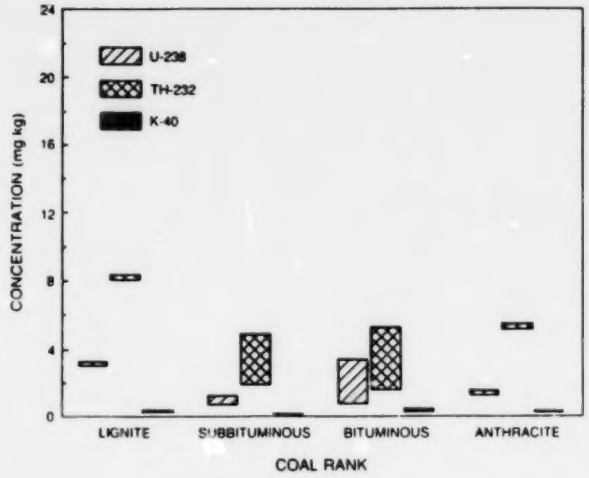

Figure 12. Variation in radionuclide concentration with coal rank for United States coals. (From Dearborn, 1985, Figure 7.)

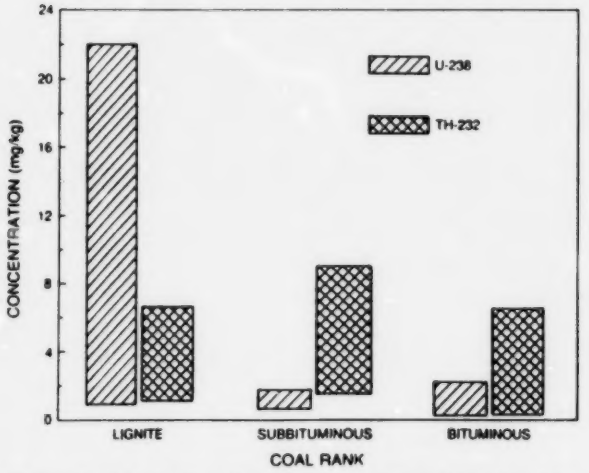

Figure 13. Variation in radionuclide concentration with coal rank for Canadian coals. (From Dearborn, 1985, Figure 8.)

concentrations, they may have significant environmental consequences. Ash currently emitted from power generating stations in Canada, including the Poplar River generating station, contains 1.0–3.0 pCi/g (37–111 mBq/g) of Th-232. However, the Poplar River generating station emission of U-238 is markedly higher than, for example, U-238 emission at the Lingan station in Nova Scotia.

Lead-210 and Po-210 are both volatile and potentially soluble nuclides. At the Poplar River generating station, the average concentration of Pb-210 in water liberated from hydrated ash deposits is about 0.4 pCi/L (14.8 mBq/L). This is significantly higher than levels reported by Evans et al. (1985) in the Cookson Reservoir, i.e., 0.063 pCi/L (2.2 mBq/L). Lead-210 concentrations in waters that are in contact with Poplar River fly ash are about a factor of 200 below the applicable standard for continuous release in the United States. Nevertheless, these results suggest that radionuclides are being environmentally redistributed in the vicinity of the power generating plant.

The extent of redistribution of nuclides within the environment can be traced using information obtained from uranium disequilibrium studies. Following the discovery of isotopic disequilibrium between U-234 and U-238 in ground- and surface-water samples by Cherdynstev et al. (1955), a vast amount of information has been accumulated about uranium disequilibrium (Osmond and Cowart, 1976), in particular, the relationship between activity ratio (AR), i.e., U-234/U-238, and uranium concentration. Activity ratios for ground-water uranium as high as 15.6 and 40.7 have been reported by Szabo (1982) and Gilkeson et al. (1983), respectively.

Enhanced ratios are considered to result from direct alpha recoil of Th-234 across the rock-water interface (Kigoshi, 1971). Thorium-234 ($t_{1/2}$ = 24.1 days) decays to U-234, enriching the ground water. Preferential leaching of U-234 atoms is an alternative mechanism which requires that U-234 atoms be more soluble than U-238 atoms. Self-oxidation could explain the selective leaching of U-234 relative to U-238 (Rosholt et al., 1965) as the aqueous solubility of U in the +5 and +6 valence state is significantly greater than in the +4 state (Langmuir, 1978). Raabe et al. (1973) have suggested that radiation damage during alpha-decay is the primary cause of preferential leaching of U-234. Enhanced ratios in ground water, therefore, reflect the combined effect of U-234 decay, recoil, and preferential leaching.

A number of studies have been undertaken on the relationship between U concentration and U-234/U-238 ratios in ground waters (see, for example, Osmond and Cowart, 1976, 1981; Cowart and Osmond, 1980; Chatham et al., 1981). Cowart and Osmond (1980) have suggested that plots of U-234/U-238 against U could be used to relate ground-water evolution to distance from sites of uranium accumulations. This approach, however, is reported by Chatham et al. (1981) to be unsuccessful in reduced ground waters because concentrations of soluble U are generally less than 1 μg/L. As uranium concentrations are relatively high in ground waters from southern Saskatchewan, Cowart and Osmond's (1980) fence diagrams, which

Table 11. Concentrations and Activities of ^{238}U, ^{232}Th and ^{40}K in Canadian Coals

^{238}U		^{232}Th		^{40}K		Coal Source and Rank A–Anthracite B–Bituminous S–Sub-bituminous L–Lignite	Reference
Conc. (mg/kg)	Activity (Bq/kg)	Conc. (mg/kg)	Activity (Bq/kg)	Conc. (mg/kg)	Activity (Bq/kg)		
1.89	(23.7)	2.5 to 3.8	(10.4 to 15.5)			B.C. Hat Creek–S/L	Dearborn (1982)
0.6 to 1.6	(7.8 to 19.6)	1.3 to 2.0	(5.2 to 8.1)			B.C. East Kootenay–B	Dearborn (1982)
0.5 to 1.7	(6.3 to 21.8)	1.59 to 9.0	(5.9 to 36.6)			Alberta Plains–S	Dearborn (1982)
1.2 to 2.0	(14.4 to 25.5)	0.9 to 6.5	(3.7 to 26.6)			Alberta Foothills–B	Dearborn (1982)
0.8 to 2.9	(10.0 to 36.6)	1.0 to 6.6	(4.1 to 27.0)			Sask-Estevan–L	Dearborn (1982)
<0.1 to 1.0	(<1.3 to 12.2)	0.2 to 6.1	(0.7 to 24.8)			Sydney, N.S.–B	Dearborn (1982)
1.2 to 2.2	(15.5 to 27.8)	1.9 to 5.5	(7.8 to 22.6)			Pictou & Cumberland, N.S.–B	Dearborn (1982)
1.2 to 1.6	(14.8 to 19.6)	1.1 to 3.6	(4.4 to 14.8)			N.B. Minto–B	Dearborn (1982)
2.9 to 11.0	(36.2 to 138.6)					Saskatchewan–L	MacCormack (1979)
0.78	(10.0)					Alberta–S	MacCormack (1979)
1.4	(17.8)	5.3	(21.5)			B.C.Hat Creek–S/L	B.C. Hydro (1981)
1.2	(15.2)	2.3	(9.3)			Alta-Luscar–B	Curtis (1980)
1.3	(16.3)	2.9	(11.8)			Byron Creek–B	Curtis (1980)
(1.0)	12.4	(1.9)	7.5	(0.11)	26.4	50/50 U.S. Appal & Western Canadian used at Nanticoke–B	Tracy and Prantl (1981)
0.7	(8.9)	1.4	(5.6)	0.14	(35.2)	Lakeview G.S. Eastern U.S. Coal–B	Muller and Bagg (1981)
<1 to 17	(11.1 to 214.6)					Sask-Estevan–L	Cameron and Birmingham (1970)*
1 to 22	(14.8 to 277.5)					Sask-Willowbunch–L	Cameron and Birmingham (1970)*

Note: *Original values as U_3O_8 (urano-uranic acid) converted to U by:

$$\frac{wt.U_3}{wt.U_3O_8} \quad \frac{714g}{842} = 0.85 \times U_3O_8 = {}^{238}U$$

( ) Calculated values

(From Dearborn, 1985, Table 8.)

relate enhanced ratios to U concentration, might be applicable in establishing the extent of uranium dissolution in mine dewatering waters at Coronach and in tracing its dispersal in south-flowing surface waters in the Poplar River basin.

Helium-4, produced by the alpha decay of uranium and thorium, is another radiogenically derived nuclide that has received considerable attention in recent studies of ground-water dynamics. Measurement of He-3/He-4 isotopic ratios for dissolved helium in ground waters has enabled the calculation of residence times of ground waters within aquifers (see Andrews and Lee, 1979; Andrews et al., 1982; Bottomley et al., 1984). However, multichronometric studies of ground-water age have shown that helium ages are commonly greater than the age obtained from the C-14 technique (Andrews and Lee, 1979; Andrews et al., 1982), possibly as a result of open system behaviour and the addition of radiogenic helium from another source. Assumptions upon which the reliability of helium-4 ages are based are summarized in Bottomley et al. (1984).

ENVIRONMENTAL IMPACT OF COAL-DERIVED CONTAMINANTS IN WATERS OF THE POPLAR RIVER VALLEY

Water Use in the Poplar River Valley

In the Poplar River valley, the principal use of water is for agricultural purposes. A number of small reservoirs have been constructed for watering livestock, and ground water is used for irrigation of alfalfa, hay, wheat, and barley. Irrigation is widespread especially between the Fort Peck Indian Reservation and the United States-Canadian border and is reported to account for 70% of the water used in this part of the basin. Water from the Poplar River system is also used for domestic supply in Coronach (Saskatchewan) and in Scobey (Montana). The Poplar River basin also supplies water for rural household consumption and garden irrigation (International Poplar River Water Quality Study, 1979a).

Biological Resources in the Poplar River Valley

Biological resources in the Poplar River system include aquatic plants, invertebrate fauna, fish, water fowl, and ungulates (International Poplar River Water Quality Study, 1979a). As many of these form part of the human food chain, the potential impact of dewatering on the quality of surface- and ground-water supplies in the Poplar River valley during mining of the Hart coal seam must be fully evaluated.

Effect of Coal-Derived Trace Elements and Radionuclides on the Environment

Trace elements, including toxic heavy metals and radionuclides, once released into the environment can be concentrated by both plants and animals, possibly with severe ecological consequences. If these form part of the food chain for humans, they are a potential health hazard. Therefore, in environmentally sensitive areas such as the Poplar River valley, principal concerns are *(a)* build-up of toxic element levels in soil, sediment, surface water, and ground water, and *(b)* the long-term effects of biological accumulation of trace elements.

Trace element contaminants in the environment influence plants and animals, either directly or indirectly. Although many trace elements are

Table 12. Radionuclide Concentrations (pCi/g) in Coal from the Poplar River and Other Canadian Localities with Comparative Data from Beck (1980)

Species	Poplar River	Battle River	Nanticoke	Beck
Th-232	0.63 ± 0.07	0.39	0.25 ± 0.01	0.49
Th-228	0.63 ± 0.01	0.35 ± 0.01	0.25 ± 0.01	
U-238	1.26 ± 0.14	0.42	0.59 ± 0.05	0.57
Th-230	2.5 ± 0.6	0.54 ± 0.40	<0.6	
Ra-226	1.05 ± 0.02	0.35 ± 0.01	0.34 ± 0.01	
Pb-210	1.72 ± 0.09	0.60 ± 0.07	0.39 ± 0.05	

(Modified from Evans et al., 1985, Table 6.15.)

Note: 1 pCi/g = 37 mBq/g

toxic to plants and animals, concentrations that cause this response are commonly much higher than background levels. A summary of the physical, chemical, and biological effects of selected trace elements is given in the appendix. Comprehensive reviews of the relative toxicity of trace elements and radionuclides are given in Bowen (1979), Gough et al. (1979), Swanson (1982), Tracy and Prantl (1985), and Dearborn (1985).

The behaviour of trace elements in terrestrial and aquatic environments is extremely complex (Bowen, 1979). Concentrations of trace elements in solution are regulated to a considerable extent by biogeochemical processes. However, the chemical form of elements in the environment (soil water, ground water, lakes, and rivers) is strongly influenced by redox state, pH, partial pressure of O_2 and CO_2, temperature, and water hardness. Rates of mobilization and resulting bioavailability of trace elements are principally governed by soil and water pH, Eh, and elemental concentration levels and by the dynamics of surface- and groundwater systems. A summary of the relative mobilities of selected trace elements is given in Table 13. The bioavailability of many metals decreases with increasing pH.

Bioaccumulation (accumulation above normal concentrations in an organism) and biomagnification (progressive concentration through the food chain) of trace elements depends on the distribution and chemical form of the trace elements in the environment. It also depends to a large extent on the type and feeding habit of the organism. Concentration ratios (factors) for selected trace elements are given in Table 14. The aquatic invertebrates exhibit highest concentration factors for Cd, Mn, Hg, Ra (and possibly U), Ag, Tl, Th, V, and Zn. Significantly, several of these elements are relatively enriched in the Poplar River lignite (see Table 8).

Trace elements essential to normal biological functioning of organisms and the concentration of these elements in soil, fresh water, and seawater are listed in Table 15. Studies have shown that in terrestrial environments animals generally obtain necessary trace elements through their food chain and from water. Plants obtain their trace element nutrients from soil or from dust fallout on their leaves.

In aquatic environments (lakes and reservoirs), trace elements are readily precipitated and accumulate in sediments, which act as efficient "sinks" for these elements. In rivers, trace elements move with clay or organic particulates in suspension, usually during periods of maximum flow when "sinks" are distributed. Dissolved trace elements are rarely transported for significant distances (Gibbs, 1973). Carbonate and bicarbonate in soil water and ground water have been shown by Ramamoorthy and Kushner (1975) to act as extremely effective complexing ligands for certain trace elements causing immobilization of these elements.

Pathways by which several of these coal-derived trace elements could impact on the environment around the coal-fired generating stations include *(a)* dust from coal dumps, *(b)* washout from these dumps, *(c)* dust from crushing, *(d)* leakage from ash disposal lagoons, and *(e)* stack emission (Scott and Hays, 1975; Dvorak and Lewis, 1978; Blackwood and Wachter, 1978; Van Voris et al., 1985). At the Poplar River generating station, a possible additional pathway that needs to be evaluated is dewatering water from the lignite aquifer, which is pumped to the surface as part of the mining process of lignite mining.

Table 13. Relative Mobilities of Selected Metals[a]

	Environmental Conditions			
Relative mobility	Oxidizing aerobic	Acid	Neutral to alkaline	Reducing anaerobic
High	Zn, As	Zn, Cu, Ni, Hg, As		
Medium	Cu, Ni, Hg, Cd	Cd	Cd, As	
Low	Pb	Pb, Mn	Pb, Mn	Mn
Very low to immobile	Mn, Cr	Cr	Cr, Zn Cu, Ni, Hg	Cr, Zn, Cu, Ni, Hg, Cd, Pb, As

[a] Adapted from Brooks (1977).

(From Van Voris et al., 1985, Table 4.2.)

Table 14. Concentration Ratios of Trace Elements Based on Edible Portions [a,b]

Trace element	Terrestrial plants	Aquatic invertebrates	Fish
Antimony	1	10	1
Arsenic	4.2	333	333
Beryllium	16	10	2
Cadmium	222	2,000	200
Chromium	250	20	40
Cobalt	87	200	20
Copper	1000	1,000	200
Germanium	—	33	3,300
Lead	2	100	300
Manganese	3000	40,000	100
Mercury	26	100,000	1,000
Molybdenum	900	10	10
Nickel	331	100	100
Radium	85	250	50
Selenium	4	167	167
Silver	32	769	2
Tellurium	0.1	75	400
Thallium	4	15,000	10,000
Thorium	1	500	30
Tin	0.25	1,000	3,000
Tungsten	24	10	1,200
Vanadium	1	3,000	10
Zinc	40	10,000	1,000

[a] Data from Vaughan et al. 1975.

[b] Concentrations in fish are generally higher in the digestive tract, viscera, and skin than in the edible muscle tissue.

(From Van Voris et al., 1985, Table 4.3.)

Relative toxicities of different trace elements associated with coal-fired power stations are given in Table 16. Moderately or highly toxic elements, including B, Mo, As, and Se, may be present in high concentrations in the Poplar River lignite. In view of the lithophile nature and radioactivity of U, Ra, and Th and their decay products, they also have high toxicity. Van Voris and Tolle (1979) have shown that the relative toxicity of different elements in solution is controlled by the physical and chemical form of the element, by environmental chemical factors, and by biotic variables.

Therefore, in assessing the possible environmental impacts of trace elements released during mining and electricity generation, it is important to consider the following factors: soil acidity, rainfall, soil depth, soil pH, vegetation and land use, and the nature of the source of the trace elements. In a pilot study of the effects of fume or ash emissions at the Poplar River generating station, Van Voris et al. (1985) concluded that Cu, Pb, Zn, V, As, Mo, and Se would not be expected to have any serious effect on plants or animals in the area, in spite of the fact that these elements are present in relatively high concentrations in the lignite fuel. The basis for this conclusion was that soils in the area are alkaline, and trace elements would be immobilized due to adsorption onto soil colloids.

Comparatively little information is currently available concerning the trace element composition of the lignite dewatering waters. In view of the U content of the coal, it is likely that they could show significant enrichment in U-238 decay products.

ENVIRONMENTAL BEHAVIOUR OF URANIUM AND THORIUM

Behaviour of Uranium

A comprehensive review of the chemistry and environmental behaviour of uranium is given in Sheppard (1980). Its behaviour is strongly influ-

Table 15. Trace Elements Essential to Plants and Animals

Element	Mean Concentration (mg/kg)			Remarks
	Soil	Fresh water	Seawater	
Boron	20	0.015	4.4	essential for blue-green algae, diatoms, seed plants
Chromium	70	0.001	0.0003	known to be essential for mammals (as Cr^{3+})
Cobalt	8	0.0002	0.00002	essential for all organisms, except perhaps to green algae and seed plants; in Vitamin B_{12}
Copper	30	0.003	0.00025	essential for all organisms
Fluorine	200	0.1	1.3	probably essential for mammals
Iodine	5	0.002	0.06	essential for corals, sponges, ascidians, vertebrates, and possibly seed plants
Iron	46000	0.5	0.002	essential for all organisms
Manganese	1000	0.008	0.0002	essential for all organisms
Molybdenum	2	0.0005	0.01	essential for all organisms
Nickel	50	0.0005	0.00058	essential for some microbes and plants, and for all vertebrates
Selenium	0.4	0.0002	0.0002	essential for some microbes and plants, and for all vertebrates
Tin	4	0.000009	0.000004	probably essential for vertebrates
Strontium	250	8	0.07	probably essential for mammals
Vanadium		0.0005	0.0025	essential for some ascidians, all vertebrates, and to some microbes and seed plants
Zinc	90	0.015	0.0049	essential for all organisms

Note: Extracted from Bowen (1979).

(From Van Voris et al., 1985, Table 4.4.)

enced by the chemistry and organic content of the soil profile and also by soil-water and ground-water chemistry. Studies have shown that, in soils, uranium either migrates to the root-mass of plants or, alternatively, is leached into the ground-water system (Sheppard, 1980). Disequilibrium between U-234 and U-238 is commonly observed within this environment. The presence of humus within the upper portion of the soil profile commonly results in the development of significant concentrations of U. According to Titaeva (1967) and Szalay (1964), under oxidizing conditions U becomes bound to organic matter as a result of ion exchange reactions, dominantly sorption and reduction of U^{6+} to U^{4+}. A number of studies have been undertaken concerning the retention of U in soil. Principal factors are mineralogy and the surface area of soil particles (see, for example, Megumi and Mamuro, 1977). These authors also showed that the concentration of U and other radionuclides in soil is influenced by Fe and Mn oxides, which reduce U^{6+} to U^{4+}.

The transport of U in solution or associated with particulate matter in the soil profile is influenced by hydrological processes that affect the movement of soil water. These include gravitational or capillary flow as well as horizontal migration. In arid and semiarid areas, like parts of the Poplar River basin, uranium is commonly concentrated at the surface of the soil profile by seasonal runoff (stream flow) and evaporation cycles (Sheppard, 1980).

The concentration of U within plants is quite variable. As a rule, plants concentrate U in their root mass (Tracy et al., 1983). However, the bioaccumulative ability of different species of plants is also variable. For example, the primitive plants (mosses, algae, and microorganisms) tend to accumulate more U than the more evolved plants. A detailed discussion of the biochemical behaviour of U, Ra-226, and Pb-210 in plants is given in Sheppard (1980) and Tracy et al. (1983).

Table 16. Potential Toxicity of Trace Elements Released from Coal-Fired Power Plants[a]

Element	Terrestrial		Aquatic
	Plant	Animal	
As	Low	Low	Low
B	High	Medium	Low[b]
Be	Medium	High	High[b]
Bi	Medium	Low	Low[b]
Cd	High	High	High
Co	High	Medium	High
Cr	High	Medium	Medium
Cu	High	Medium	High
F	High	High	Low
Hg	Medium	High	High
Mn	Low	Low	Low
Mo	Low	Medium	Low
Ni	High	High	Medium
Pb	Low	Medium	Medium
Sb	Medium	High[b]	Low[b]
Se	Medium	High	Low[b]
Sn	Low	Low	Low
Ti	Low	Low	Medium[b]
Tl	High	High	Medium[b]
V	High	Low	Medium[b]
W	Medium	Medium[b]	Low[b]
Zn	Low	Medium	Medium

[a] Adapted from Jones (1978).
[b] Uncertain.

(From Van Voris et al., 1985, Table 4.5.)

Although comparatively little information is known about the chemical toxicity and radiological tolerance of plants (Sheppard, 1980), radiation injury to root systems has been reported in soils with U activity of 0.1 μCi/g (3700 Bq/g) (Jacobson and Overstreet, 1948).

Behaviour of Thorium

The thorium content of soils is highly variable, ranging between 2.3 and 1000 mg/kg (Nishita et al. 1978). However, the behaviour of Th is somewhat different from U, with low concentrations being reported from organic-rich horizons and higher concentrations near the soil-regolith boundary (Sheppard, 1980). The distribution of Th within soil profiles is influenced by variations in the geochemical behaviour of U-238 decay products, i.e., Th-234 to U-234 to Th-230 (Fig. 11). This commonly results in disequilibrium between Th-230 and U-234 as a result of preferential leaching (Hansen and Stout, 1968). As a result, top soils generally contain higher abundances of U-234, whereas Th-230 is more abundant lower in the soil profile. Reactions between Th and soil have been reviewed by Rancon (1973). The principal reactions are *(a)* adsorption of Th onto organic soils under neutral to slightly acidic conditions, *(b)* adsorption onto clay from dilute solutions with pH values >2, and *(c)* precipitation of $Th(OH)_4$ due to calcareous buffering. Solution transport of Th is considered to be a relatively unimportant process; most movement of Th through soil takes place by means of a particulate transport, possibly colloidal (Sheppard, 1980).

Studies of the effect of pH and elemental concentration on Th partitioning in soils have been carried out by Rancon (1973). Conclusions pertinent to the potential behaviour of Th in Poplar River basin soils are *(a)* that K_d's are low in alkaline soils because of the dissolution of humic acid, which complexes Th, and *(b)* that calcareous soils tend to concentrate Th by means of the precipitation of $Th(OH)_4$ (Sheppard, 1980).

Information concerning the distribution of Th in plant tissue presented in Sheppard (1980) indicates that the sites of concentration of Th are

largely dependent on species. Considerable variation in isotopic ratios has also been reported within plants. This variation is considered to be due to isotopic disequilibrium within the soil profile (Titaeva et al., 1978).

There is little information available regarding the distribution of Th in soils, surface waters, or ground waters in the Poplar River basin.

BIOACCUMULATION OF RADIONUCLIDES

Comprehensive literature studies on the environmental behaviour of radionuclides have been undertaken by Patzer (1976) and Swanson (1982). The literature review by Swanson (1982) also provides a concise assessment of the radiotoxicity of radionuclides. Radionuclides produced by the natural decay of Th and U that are introduced into the environment through the water cycle either remain in solution or are transported by means of particulate matter. The environmental behaviour of radionuclides appears to be strongly influenced by variations in nuclidic mobility that results in disequilibrium relationships between isotopes. Under certain circumstances, radionuclides are immobilized in environmental "sinks," or alternatively they may be concentrated by plants and animals. The concentration of some radionuclides is related to the chemical similarity of a particular nuclide to an essential nutrient, e.g., Ra-226 and Ca. This does not appear to be the case with U, however, and passive uptake appears to be the dominant process (Swanson, 1982).

Factors that govern the concentration of specific radionuclides in terrestrial and aquatic biota are *(a)* its chemical form and behaviour, *(b)* its concentration, *(c)* its chemical similarity to essential nutrients, *(d)* its transport mechanism within the environment, and *(e)* the location within the environment of the concentration organism or organisms and their physiology (Swanson, 1982). However, only limited information is available on bioconcentration in the literature, and the bioconcentration factors are quite variable (Letourneau, 1987). It is generally recommended that site-specific studies be carried out to assess the impact of any new developments, such as lignite mining and use in the Poplar River basin.

Significant information on the cycling of radionuclides in the environment can be provided by aquatic organisms because of their concentrating ability. Such organisms ultimately provide *(a)* information on the behaviour of radionuclides in the food chain, *(b)* spatial information regarding the distribution of radionuclides in nature, and *(c)* a means of monitoring the effect of radionuclides within the environment.

Information regarding the concentration of radionuclides near coal-fired power stations clearly indicates the presence of enhanced levels in fuel used in some stations, e.g., Poplar River lignite. This relationship principally exists because of the concentrating capacity of fly ash (MacCormack, 1979). In a study of the radiological effect of coal-fired power generation at the Nanticoke thermal generating station and an ash disposal site in metropolitan Toronto operated by Ontario Hydro, Tracy and Prantl (1985) concluded that *(a)* there was no evidence of enhancement of radionuclide levels from station emissions, and *(b)* leaching of radionuclides or diffusion of radon gas from ash disposal sites had minimal environmental effects. However, higher than background radiation levels were reported from fly ash used in building materials. As coal used in the Nanticoke thermal generating station is particularly unradiogenic (Tables 11 and 12), the universal application of these results remains to be tested in an environment such as the Poplar River valley where U-bearing lignite is used as a fuel. This is because the bioaccumulative effects of coal-derived radionuclides to terrestrial and aquatic food chains, reviewed in Swanson (1982), show this to be a potential area of environmental concern.

CONCLUSIONS

From this literature review, it is apparent that there are a number of deficiencies in the information base concerning the possible environmental effects of aquatic discharges associated with lignite mining and its subsequent use in the Poplar River basin. Thus, information is needed in several areas.

Information Gaps

1. The chemistry of ground water in the Coronach area. Data for waters need to include pH, Eh, and concentration data for the major cations, anions, and trace elements (particularly those known to be concentrated in the lignite, e.g., B, Th, U, Mo, S, As, and Se), and radiochemical data for U-238 and Th-232 decay products.

2. The above chemical data on surface waters, especially those influenced by the flux of dewatering water.

3. Major element, trace element, and radionuclide chemistry of soil profiles, aquifer lithologies, with particular emphasis being placed on data from the Hart coal seam and fly ash concentrations.

4. U-234/U-238 versus U concentration data for surface and ground water.

5. An assessment of thermodynamic data for actinides below 20°C to model the behaviour of U dissolution and precipitation.

6. Data on partitioning of U and Th between soil and ground water, e.g., determination of partition coefficients.

7. Transport mechanisms for U and Th derived from the lignite seams or fly ash lagoons.

8. Trace element and radiochemical concentration levels in different species of aquatic organisms and stream, lake, and reservoir sediments in the Poplar River valley.

9. Trace element and radiochemical concentration levels in natural plant communities in the Poplar River valley.

10. Ecotoxicological and ecoradiological data concerning U and Th, and their daughter isotopes, in the ecosystems of the Poplar River valley.

A logical extension of this assessment would be a comprehensive study of the levels of Th and U, and the radiochemistry of their daughter products in ground waters from the Cypress Hills, where lignite horizons contain significantly higher concentrations of U than in the Coronach area.

Immediate Information and Research Needs

The Hart coal seam is currently being mined to fuel the Poplar River thermal generating station at Coronach. Very few data are publicly available concerning the trace element and radionuclide concentrations in the dewatering water and the lignite. Also, lignite burning at the power plant produces large quantities of ash, which is likely to concentrate both trace elements and radionuclides.

The underlying question is whether or not the lignite mining and its subsequent use has affected the water quality in the Poplar River. To answer this question, research and monitoring should be undertaken in the following areas:

1. Determine the quality of the river water before it enters the Cookson Reservoir to establish baseline conditions. Parameters of concern would primarily be the trace element and the radionuclide concentrations.

2. Analyze dewatering water, lignite, and ashes to establish input sources.

3. Determine the quality of water leaving the Cookson Reservoir, preferably at the Canada-U.S. border.

4. If possible, analyze biota and sediments in the Poplar River at several locations, i.e., above, inside, and downstream from the Cookson Reservoir.

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Appendix

Physical, Chemical and Biotic Properties of Trace Elements (from Van Voris et al., 1985)

APPENDIX A

PHYSICAL, CHEMICAL AND BIOTIC PROPERTIES OF TRACE ELEMENTS[a]

Antimony (Sb)

- MPC-FW(EPA 1976) for aquatic life: acute 9.0 mg/l, chronic 1.6 mg/l (Sittig 1981)
- mean natural concentrations in soil, 1 mg/kg; in freshwater, 0.0002 mg/kg; and in sea water, 0.00024 mg/kg (Bowen 1979)
- moderately toxic to all organisms (CWQC 1973)
- limited knowledge on aquatic effects or fate (BCHPA 1980), 100 mg/day is toxic to people
- limited bioconcentration
- not biomagnified in food chains, relatively immobile.

Arsenic (As)

- MPC-FW(EPA) for aquatic life: 0.44 mg/l as recoverable trivalent inorganic As (Sittig 1981)
- ECIWD ≤ 0.05 mg/l (EC 1979)
- mean natural concentration in soil, 6 mg/kg; in freshwater, 0.0005 mg/kg; and in sea water, 0.0037 mg/kg (Bowen 1979)
- moderately toxic to animals; toxicity varies widely with chemical form and oxidation state (Thurston et al. 1979)
- bioaccumulated by fish from food and water (Vaughan et al. 1975, BCHPA 1980) but depuration fairly rapid (Sorenson 1976)

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[a] Adapted from Bowen 1979, Dvorak and Lewis 1978, and Vaughan et al. 1975.
Definitions:
MPC-FW = Maximum Permissible Concentration in Freshwater (United States criteria).
EPA = United States Environmental Protection Agency
FW = freshwater.
ECIWD = Environmental Canada Internal Water Directorate (Canadian Criteria).
EC = Environment Canada.
AFS = American Fisheries Society.
CWQC = Committee on Water Quality Criteria.
BCHPA = British Columbia Hydro and Power Authority.

- limited biomagnification through food chain (Penrose et al. 1977)
- exists as arsenates (As^{5+}) in oxidizing conditions, arsenites (As^{3+}) in moderate reducing conditions (Thurston et al. 1979)
- has been associated with increased incidence of lung cancer
- arsenite (As^{3+}) is for more toxic than arsenate (As^{5+}) (Braunstein et al. 1977, Ferguson and Gavis 1972, Lambow and Lim 1970)
- may be methylated in soils and sediments to less toxic form (Peoples 1975); methylated form is readily oxidized
- combines with sulfide in sediments to form stable solids.

Barium (Ba)

- MPC-FW (EPA) for aquatic life, none; for domestic water supplies, 1.0 mg/l (Sittig 1981)
- mean natural concentrations in soil, 500 mg/kg; freshwater, 0.01 mg/kg; and sea water, 0.013 mg/kg (Bowen 1979)
- solubility of Ba is controlled by $BaSO_4$ or $BaCO_3$ (Butler 1964)
- limited toxicity at concentrations ≤ 50 mg/l (CWQC 1973)
- limited knowledge on aquatic effect or fate
- bioaccumulated, but not biomagnified, by aquatic organisms (BCHPA 1980); poorly absorbed with generally little retention in mammalian tissues.

Beryllium (Be)

- MPC-FW(EPA) for aquatic life: acute 0.130 mg/l, chronic 0.0053 mg/l (Sittig 1981); toxic to plants at 0.5 mg/l and very toxic to terrestrial mammals
- mean natural concentration in soil, 0.3 mg/kg; freshwater, 0.0003 mg/kg; and sea water, 0.0056 µg/kg (Bowen 1979)
- primarily in dissolved form at < 0.001 mg/l in freshwater; sediments usually with 2-3 mg/l (Drury et al. 1978)
- chloride, nitrate and sulfate salts are water soluble; carbonate and hydroxide are nearly insoluble in cold water
- more soluble in acidic than in neutral or alkaline water
- Be ion lowers pH via hydrolysis; under some conditions, forms complexes leading to precipitation, e.g., very hard water at pH 5-7, or in buffered solutions above pH 5.0 (Slonim 1971)
- bioaccumulated by fish in relation to concentration in water (Slonim and Damm 1972); known to cause granulenteous changes in lung tissue

- readily excreted, hence, not biomagnified (BCHPA 1980, Vaughan et al. 1975)
- more toxic in soft than in hard water, possibly because of antagonism with Ca (Slonim and Slonim 1973, Thurston et al. 1979)
- limited knowledge on aquatic effects or fate.

Boron (B)

- MPC-FW (EPA) for aquatic life, none; for human health, 0.043 mg/l (Sittig 1981); essential to plant growth < 4 mg/kg
- mean natural concentration in soil, 20 mg/kg; freshwater, 0.015 mg/kg; and sea water, 4.4 mg/kg (Bowen 1979)
- essential element for blue-green algae, diatoms and seed plants (Bowen 1979)
- relatively nontoxic to freshwater fish; however, very toxic to plants when available B > 30 mg/kg (Thurston et al. 1979, Adriano et al. 1980)
- uptake is related to bioavailability; apparently not retained or bioaccumulated by invertebrates but retained by plants (Thompson et al. 1976).

Cadmium (Cd)

- MPC-FW(EDA) for aquatic life: e[1.05 ln(hardness) - 8.53] µg/l, not to exceed e[1.05 ln(hardness)-3.73] µg/l over 24 hr (Sittig 1981); toxic to plants 0.2-9 mg/l (Bowen 1979)
- ECIWD, 0.0002 mg/l as total Cd (EC 1979)
- AFS recommended criteria for sensitive/less sensitive aquatic species varies with hardness (Thurston et al. 1979):

hardness (mg/l $CaCO_3$)	Cd mg/l
0.35	0.4/0.8
35-75	1.0/2.0
75-150	2.5/5.0
150-300	6.0/12.0
> 300	15.0/30.0

- mean natural concentration in soil, 0.35 mg/kg; freshwater, 0.0001 mg/kg; and sea water, 0.00011 mg/kg (Bowen 1979)
- elemental Cd is insoluble in water; chloride, nitrate and sulfate forms are highly soluble (Schneider 1971)
- ionic activity decreases with a rise in pH, or an increase in hydroxide or carbonate activity (Thurston et al. 1979)

- toxic to fish at low concentrations, teratogenic (Thurston et al. 1979, BCHPA 1980)
- readily bioaccumulated and slowly excreted by fish (Kumada et al. 1973, Phillips and Russo 1978)
- high concentrations occur in benthic organisms (Mathis and Cummings 1973)
- may biomagnify through food chain, but evidence limited
- less toxic in hard water, apparently due to antagonism with Ca and possibly Mg (Hutchinson and Czyrska 1972, Davies 1976)
- toxicity enhanced by Zn, lowered by Se, and enhanced and/or lowered by Pb (Davies 1976, Reeder et al. 1979a).

Chromium (Cr)

- MPC-FW(EPA) for aquatic life: trivalent Cr $\leq$ e[1.08 In(hardness) + 3.48] µg/l, hexavalent Cr $\leq$ 21.0 µg/l or 0.29 µg/l as 24-hr mean (Sittig 1981)
- ECIWD, 0.04 mg/l as total Cr (EC 1979)
- mean natural concentrations in soil, 70 mg/kg; freshwater, 0.001 mg/kg; and sea water, 0.0003 mg/kg (Bowen 1979)
- essential to mammals in trivalent form (Cr^{3+})
- relatively toxic to aquatic life; hexavalent Cr (Cr^{6+}) is main toxic form (Taylor et al. 1979), but trivalent Cr (Cr^{3+}) is usually prevalent in water (Schroeder and Lee 1975)
- Cr^{3+} forms stable complexes with negatively-charged inorganic and organic materials (Taylor et al. 1979)
- causes sublethal effects on fish and aquatic invertebrates at low concentrations
- aquatic invertebrates are usually more sensitive than fish (Thurston et al. 1979)
- moderately bioaccumulated by aquatic organisms (Phillips and Russo 1978), but rapidly eliminated (Knoll and Fromm 1960, Buhler et al. 1977); accumulates in trees
- no present data indicate biomagnification through the aquatic food chain (BCHPA 1980)
- toxicity to aquatic life affected by hardness, pH, and ionic state (Cr^{3+} or Cr^{6+}); 0.5-10 mg/Cr(VI)/l toxic to plants, 200 mg/day toxic to people.

Cerium (Ce)

- MPC-FW(EPA), no criteria (Sittig 1981)
- mean natural concentrations in soil, 50 mg/kg; freshwater, 0.0002 mg/kg; and sea water, 0.0012 µg/kg (Bowen 1979)
- radioisotopes ($t_{\frac{1}{2}}$) ^{141}Ce (33 days), ^{144}Ce (284 days) f.p. (Bowen 1979).

Cesium (Cs)

- MPC-FW(EPA), no criteria (Sittig 1981)
- mean natural concentrations in soil, 4 mg/kg; freshwater, 0.00002 mg/kg; and sea water, 0.0003 mg/kg (Bowen 1979)
- relatively harmless trace element
- radioisotopes ($t_{\frac{1}{2}}$) ^{134}Cs (2.1 yr), ^{137}Cs (30 yr) (Bowen 1979).

Cobalt (Co)

- MPC-FW(EPA) suggested limit based on health effects 0.7 µg/l (Sittig 1981)
- mean natural concentrations in soil, 8 mg/kg; freshwater, 0.0002 mg/kg; and sea water 0.00002 mg/kg (Bowen 1979)
- radioisotopes ($t_{\frac{1}{2}}$) ^{60}Co (5.3 yr) (Bowen 1979)
- essential to all organisms, except perhaps green algae and seed plants (Bowen 1979); present in Vitamin B_{12} (Sittig 1981)
- associates with particulate matter and sediments in freshwater, becoming unavailable for bioaccumulation (Phillips and Russo 1978)
- Co bioaccumulates in soft tissues of freshwater organisms (Brungs 1967), but depuration is rapid (BCHPA 1980); when low in soil, grazing animals typically are negatively affected
- uptake of Co by trout eggs decreases as Ca content increases (antagonistic) (Kunze et al. 1978).

Copper (Cu)

- MPC-FW(EPA) for aquatic life, 5.6 µg/l as 24-hr average and not to exceed e[0.94 ln(hardness)-1.23] µg/l (Sittig 1981); 0.5-8 mg/l toxic to plants, 250 mg/day toxic to people
- mean natural concentration in soil, 30 mg/kg; freshwater, 0.003 mg/kg; and sea water 0.00025 mg/kg (Bowen 1979)

- essential element to all organisms
- metallic Cu is insoluble in water, but many salts are highly soluble as cupric (Cu^{+1}) or cuprous (Cu^{2+}) ions (Schneider 1971)
- cupric ions added to natural water of ≥ 7.0 quickly precipitate as copper hydroxide or as basic copper carbonate (Braunstein et al. 1977)
- Cu is complexed and held in solution by organic material in hard water (Brown et al. 1974)
- toxicity to aquatic organisms varies widely with temperature, turbidity, hardness and CO_2 content (Thurston et al. 1979, BCHPA 1980)
- toxic to fish, highly toxic to aquatic invertebrates, particularly to algae and molluscs (Thurston et al. 1979)
- readily bioaccumulated by lower plant forms like Bryophates, known to be accumulated by fish and aquatic insects, sometimes to toxic levels (Phillips and Russo 1978, BCHPA 1980); readily depurated
- enriched in sediments, concentrations usually 1-476 mg/kg (Leland et al. 1978)
- decreases in hardness, and pH (acidity) increases the toxicity of Cu (Thruston et al. 1979, BCHPA 1980)
- Zn, Cd and Hg increase toxicity of Cu to aquatic life (synergistic) (Corner and Sparrow 1956, Lloyd 1961b, MacInnes and Thurberg 1973).

Dysprosium (Dy)

- MPC-FW(EPA) for aquatic life, none (Sittig 1981)
- mean natural concentrations in soil, 5 mg/kg; freshwater, 0.000005 mg/kg; and sea water 0.00091 µg/kg (Bowen 1979)
- low toxicity.

Europium (Eu)

- MPC-FW(EPA) for aquatic life, none (Sittig 1981)
- mean natural concentrations in soil, 1 mg/kg; freshwater 0.000006 mg/kg; and sea water, 0.00013 µg/kg (Bowen 1979)
- radioisotopes ($t_{\frac{1}{2}}$), ^{152}Eu (12 yr), ^{155}Eu (1.8 yr) (Bowen 1979)
- low toxicity.

Fluoride (F)

- MPC-FW(EPA) for aquatic life, none (Sittig 1981)
- mean concentration in soil, 200 mg/kg; freshwater, about 0.01 to 0.02 mg/kg (Carpenter 1969), or 0.1 mg/kg and sea water, 1 - 3 mg/kg (Bowen 1979)
- probably an essential element for mammals (Bowen 1979), but not for plants
- in gaseous form, particularly as HF, toxic to emergent and riparian plants (Groth 1975)
- F in solution is readily absorbed by plants
- low toxicity to fish compared to heavy metals
- little information of acute or chronic effects to aquatic life (BCHPA 1980)
- bioaccumulated by fish, primarily in skeleton (Wright 1977).

Gold (Au)

- MPC-FW(EPA) for aquatic life, none (Sittig 1981)
- mean natural concentrations in soil, 0.001 mg/kg; freshwater, 0.000002 mg/kg; and sea water 0.004 µg/kg (Bowen 1979)
- scarcely toxic (Bowen 1979).

Iodine (I)

- MPC-FW(EPA) for aquatic life, none (Sittig 1981)
- mean natural concentrations in soil, 5 mg/kg; freshwater, 0.002 mg/kg; and sea water, 0.06 mg/kg (Bowen 1979)
- essential trace element for many marine invertebrates, possibly other aquatic organisms (Bowen 1979); required by fish (Piper et al. 1982)
- accumulates in red and brown algae and their marine predators.

Iron (Fe)

- MPC-FW(EPA) for aquatic life, 1.0 mg/l (Sittig 1981)
- mean natural concentrations in soil, 40,000 mg/kg; freshwater, 0.5 mg/kg; and sea water, 0.002 mg/kg (Bowen 1979)
- essential element for all organisms (Bowen 1979)

- relative low toxicity to aquatic organisms (Thurston et al. 1979), 10-200 mg/l toxic to plants (Bowen 1979)
- Fe exposed in surface water oxidizes to hydrated ferric oxide, which is less soluble than Fe^{2+} and Fe^{3+} (Thurston et al. 1979)
- Fe accumulates in sediments as black mineral muds
- can combine with soluble phosphate, to eliminate phosphorus as a nutrient for aquatic plants (Willson 1973)
- possible synergistic when combined with other metals, especially at low pH (Thurston et al. 1979).

Lead (Pb)

- MPC-FW(EPA) for aquatic life, e[2.35 ln(hardness) - 9.48], not to exceed e[1.22 ln(hardness) - 0.47] (Sittig 1981); 3-20 mg/l toxic to plants, 1 mg/day toxic to people, 10 mg/day lethal to people
- AFS recommended criteria for freshwater organisms varies with hardness (Thurston et al. 1979):

hardness (mg/l $CaCO_3$)	Pb µg/l
0 - 30	0.004
30 - 100	0.025
100 - 300	0.050
300	0.10

- natural concentrations in soil, 35 mg/kg; freshwater, 0.001 to 0.010 mg/l; in sediments, 5 to 810 mg/kg; and sea water 0.03 µg/kg (Leland et al. 1978)
- most Pb is precipitated in freshwater as carbonates or hydroxides; decreasing pH increases availability of Pb^{2+} (Merlini and Pozzi 1977a, 1977b)
- divalent Pb (Pb^{2+}) is main toxic form; toxic to aquatic life usually at >0.01 mg/l (Dvorak and Lewis 1978)
- relatively toxic to fish, particularly in soft water; causes sublethal effects at low concentrations
- low solubility of 0.5 mg/l in soft water and only 0.030 mg/l in hard water; water may contain colloidal and suspended Pb (Davies 1976)
- Pb is absorbed by clays, or complexed with dissolved and suspended organic materials, hence accumulates in sediments
- benthic invertebrates are impacted by high concentrations of Pb in sediments (Warnick and Bell 1969)
- methylated by microorganisms in aquatic sediments (Wong et al. 1975)

- Pb toxicity to fish and bioaccumulation decreased (antagonistic) by Ca (Phillips and Russo 1978)
- divalent form (Pb^{2+}) bioaccumulated but not biomagnified in aquatic food chain (BCHPA 1980).

Manganese (Mn)

- MPC-FW(EPA) for aquatic life, none; 50 µg/l for domestic water supplies (Sittig 1981)
- natural concentrations in soil, 1000 mg/kg; freshwater, usually <1 mg/l; and sea water, 0.0002 mg/kg (Thurston et al. 1979)
- essential trace element for all organisms
- divalent Mn (Mn^{2+}) oxidizes in surface water to the much less soluble hydrated manganese oxide (MnO_2)
- relatively low toxicity to aquatic life, with slow-acting effects (Thurston et al. 1979)
- toxicity varies widely with water quality, including hardness and pH
- Mn decreases (antagonistic) Ni toxicity to fish (NAS 1973)
- bioaccumulated by aquatic life (NAS 1973, Thompson et al. 1972, Vaughan et al. 1975).

Mercury (Hg)

- MPC-FW(EPA) for aquatic life, 0.016 µg/l (methylmercury) as a 24-hr average, never to exceed 8.8 µg/l (Sittig 1981); very toxic to plants and soil fungi, 0.4 µg/day toxic to people (Bowen 1979)
- ECIWD, 0.0001 mg/l to protect fish consumers, 0.002 mg/l to protect aquatic life (EC 1979)
- mean natural concentration in soil, 0.06 mg/kg; freshwater, 0.0001 mg/kg; and sea water, 0.00003 mg/kg (Bowen 1979)
- methylmercury is highly toxic to aquatic life, about 10X more toxic than inorganic Hg (Peakall and Lovitt 1972); acute and chronic effects (Thurston et al. 1979)
- toxicity affected by chemical form (e.g., methylmercury), temperature, DO concentration, water hardness and other metals (BCHPA 1980)
- inorganic Hg in freshwater rapidly enters the sediments where it is transformed to dimethyl or methyl Hg by microorganisms (Jensen and Jernelov 1969, Wood 1974); release from sediments is slow (Jacobs and Keeny 1974)

- also forms insoluble mercuric sulphids (HgS) in sediments by cation exchange with insoluble sulphidic minerals and reaction with bioproduced H_2S (Reeder et al. 1979b)
- the soluble methylmercury is readily bioaccumulated (Olson et al. 1975) and biomagnified in aquatic food chains; rapid uptake, slow depuration by aquatic life (D'Itri 1972, BCHPA 1980)
- Cu protects against Hg toxicity (Roales and Perlmutter 1974); Se slows uptake (synergism) of Hg by fish (Kim et al. 1977).

Molybdenum (Mo)

- MPC-FW(EPA) for aquatic life, none; for human health 70 µg/l suggested (Sittig 1981)
- concentrations in soil, 1-2 mg/kg; freshwater, from 0.3 to 0.13 mg/l (Dvorak et al. 1978), mean concentration, 0.0005 mg/kg; and sea water, 0.01 mg/kg (Bowen 1979)
- essential trace element for all organisms (Bowen 1979); required by blue-green algae to fix nitrogen (Hardy and Burns 1968)
- relatively low toxicity to aquatic life (BCHPA 1980), 0.5-2 mg/l toxic to plants, 5 mg/day toxic to mammals, can cause molybdenosis in cattle
- biologically active but does not bioaccumulate (Vaughan et al. 1975).

Nickel (Ni)

- MPC-FW(EPA) for aquatic life, e[0.76 ln(hardness) + 1.06] as a 24-hr average, never to exceed e[0.76 ln(hardness) + 4.02] (Sittig 1981)
- natural concentrations in soil, 50 mg/kg; freshwater, 0.003 to 0.08 mg/l; in sediments, 1 to 135 mg/l (Leland et al. 1978); and sea water 0.00058 mg/kg (Bowen 1979)
- essential element for some microorganisms and plants, and for all invertebrates (Bowen 1979)
- not soluble in water as a metal, but many inorganic salts are soluble (NAS 1973)
- only moderately toxic to aquatic organisms (Dvorak and Lewis 1978)
- bioaccumulated by algae, but to lesser extent than Fe, Pb and Cu (Stokes et al. 1973)
- accumulates in sediments from industrial activity (BCHPA 1980)
- may exhibit synergism when present with other metallic ions (NAS 1973).

Radium (Ra)

- mean concentration in freshwater, 4×10^{-10} mg/kg (Bowen 1979)
- natural radioisotopes ($t_{\frac{1}{2}}$): ^{226}Ra (1,622 yr), ^{228}Ra (6.7 yr) (Bowen 1979)

Selenium (Se)

- MPC-FW(EPA) for aquatic life, 35 µg/l as 24-hr average, never to exceed 260 µg/l recoverable inorganic selenite (Sittig 1981)
- natural concentrations in soil, 0.4 mg/kg; freshwater, 0.001 to 0.40 mg/l; in sediments, 0.1 to 1.0 mg/l (Adams and Johnson 1977, BCHPA 1980); sea water, 0.0002 mg/kg
- essential trace element for some microbes and plants, and to all vertebrates (Bowen 1979); required nutrient for fish (Poston et al. 1976)
- elemental Se is relatively insoluble but is slowly oxidized to SeO_2, which forms soluble selenite salts (Lakin 1973)
- Se content of surface water is higher under alkaline (pH 7.8 - 8.2) than slightly acidic (pH 6.1 - 6.9) conditions (Lakin 1973)
- may oxidize to soluble Se ion at about pH 8.0, but precipitates as basic ferric selenite at pH 6.3 - 6.7 (Lakin 1973, NAS 1973)
- complexes with suspended materials and accumulates in sediments (Dvorak et al. 1978, Thurston et al. 1979)
- acute and chronic toxicity to aquatic organisms; most fish species die in 2 wk when exposed down to 1 mg/l Se (Thurston et al. 1979); 1-2 mg Se(IV) toxic to plants, 5 mg/day toxic to people (Bowen 1979)
- Se is apparently a cumulative poison for fish, causing delayed mortality via physiologic dysfunction (Thurston et al. 1979)
- invertebrates accumulate higher Se levels than fish (Dvorak et al. 1978)
- in field situations, fish do not readily bioaccumulate Se, compared to Cu, Cd, Hg and Zn (Phillips and Russo 1978, Thurston et al. 1979)
- can be methylated in sediments by microbes (Chau et al. 1976)
- reduces effects (antagonistic) of Cd and As in higher invertebrates (Braunstein et al. 1977); may also protect against toxicity of Hg compounds (Koeman et al. 1975, Parizek 1978); enhances toxicity (synergistic) with Hg for carp eggs (Huckabee and Griffith 1974).

Silver (Ag)

- MPC-FW(EPA) for aquatic life, not to exceed e[1.72 ln(hardness) - 6.52] mg/l at any time (Sittig 1981)
- natural concentrations in soil, 0.05 mg/kg; freshwater, 0.0003 mg/kg; sea water, 0.00004 mg/kg (Bowen 1979)
- AFS recommended criteria for freshwater organisms varies with hardness (Thurston et al. 1979):

hardness (mg/l $CaCO_3$)	Ag (mg/l)
0 - 75	0.10
75 - 150	0.10
150 - 300	0.15
300 - 400	0.20
> 400	0.25

- rarely detected in freshwater above 1 mg/l (NAS 1973); mean natural concentration in freshwater 0.0003 mg/l (Bowen 1979); usually 0.5 mg/kg in sediments (Leland et al. 1978)
- most Ag compounds have limited solubility in water (Phillips and Russo 1978)
- one of most toxic metals to fungi, plants and aquatic life, but of little hazard due to low solubility
- does not bioaccumulate in fish, no biomagnification in aquatic food chain, very short biological half life (Hutchinson and Czyrska 1972, Vaughan et al. 1975).

Strontium (Sr)

- mean natural concentrations in soil, 250 mg/kg; freshwater, 0.07 mg/kg; sea water, 7-9 mg/kg (Bowen 1979)
- radioisotopes ($t_{\frac{1}{2}}$): ^{89}Sr (51 days), ^{90}Sr (29 yr) f.p. (Bowen 1979)
- scarcely toxic to plants, 8 mg/day toxic to mammals
- bioaccumulated in vertebrate bone, all brown algae (Bowen 1979).

Thallium (Tl)

- MPC-FW(EPA) for aquatic life: acute, 1,400 µg/l; chronic 40 µg/l (Sittig 1981)
- natural concentrations in soil, 0.2 mg/kg; usually undetected in freshwater; sea water 0.000019 mg/kg

- radioisotope ($t_{\frac{1}{2}}$); ^{208}Tl (3.1 min) (Bowen 1979)
- acute and chronic effects on aquatic organisms (Zitko 1975, Zitko et al. 1975, BCHPA 1980)
- bioaccumulated by fish and aquatic invertebrates (Vaughan et al. 1975)
- information on aquatic effects and fate is limited.

Thorium (Th)

- MPA-FW(EPA) for aquatic life, none (Sittig 1981)
- natural radioisotopes ($t_{\frac{1}{2}}$): ^{228}Th (1.9 yr), ^{230}Th (75 kyr), ^{232}Th (13.9 6 yr) (Bowen 1979)
- mean natural concentrations in soil, 9 mg/kg; freshwater, 0.00003 mg/kg; sea water, 0.001 ug/kg (Bowen 1979)
- readily precipitated to sediments and immobilized (Russel and Smith 1966)
- moderately bioaccumulated by fish and freshwater invertebrates (Vaughan et al. 1975)
- apparently not biomagnified in food chain (BCHPA 1980).

Tin (Sn)

- MPC-FW(EPA) for aquatic life, none (Sittig 1981)
- mean natural concentration in soil, 4 mg/kg; freshwater, 0.000009 mg/kg; and sea water, 0.004 mg/kg (Bowen 1979); about 0.001 to 0.27 mg/l (Peterson et al. 1976)
- probably essential element for vertebrates (Underwood 1975, Bowen 1979)
- inorganic Sn relatively nontoxic to most organisms, organic Sn highly toxic to mammals (BCHPA 1980)
- inorganic form may be alkylated in aquatic sediment by bacteria (Peterson et al. 1976)
- bioaccumulated by fish and freshwater invertebrates (Vaughan et al. 1975)
- relatively immobile in environment (BCHPA 1980).

Tungsten (W)

- MPC-FW(EPA) for aquatic life, none; suggested permissible goal of 14 µg/l based on health effects (Sittig 1981)

- mean natural concentrations in soil, 1-5 mg/kg; freshwater, 0.00003 mg/kg; and sea water 0.0001 mg/kg (Bowen 1979)
- radioisotopes ($t_{\frac{1}{2}}$): ^{181}W (30 days), ^{185}W (74 days) ^{187}W (1 day) (Bowen 1979)
- bioaccumulated by fish but not biomagnified in food chain (BCHPA 1980, Vaughan et al. 1975)
- rapidly depurated by fish, biological half-life about 2.75 days (Reed 1969).

Uranium (U)

- MPC-FW(EPA) for aquatic life, none; suggested permissible goal of 3 µg/l based on health effects (Sittig 1981)
- natural concentrations in soil, 2 mg/kg; in water are very low (Welford and Baird 1967); mean concentration in freshwater 0.0004 mg/kg (Bowen 1979)
- natural radioisotopes (% natural abundance: $t_{\frac{1}{2}}$): ^{234}U (0.000056:248 kyr), ^{235}U (0.0072:0.71 Gyr), ^{238}U (0.9927:4.5 Gyr) (Bowen 1979)
- bioaccumulated in aquatic organisms through food chain, particularly from water to algae, to fish (Kovalsky et al. 1967, Vaughan et al. 1975)
- moderately toxic to aquatic organisms, environmentally mobile (BCHPA 1980).

Vanadium (V)

- MPC-FW(EPA) for aquatic life, none; suggested permissible limit of 7 µg/l based on health effects (Sittig 1981)
- mean natural concentration in soil, 90 mg/kg; freshwater, 0.0004 mg/kg; and sea water, 0.0025 mg/kg (Bowen 1979)
- natural radioisotopes ($t_{\frac{1}{2}}$): ^{50}V (6×10^{15}) yr (Bowen 1979)
- essential trace element for some ascidians, all vertebrates, and some microbes and seed plants (Bowen 1979)
- generally nontoxic to animals (BCHPA 1980)
- bioaccumulated by certain marine, but not freshwater, invertebrates (Vaughan et al. 1975).

Zinc (Zn)

- MPC-FW(EPA) for aquatic life, 47 µg/l as 24-hr average, never to exceed e[0.83 ln(hardness) + 1.95] µg/l (Sittig 1981)

- AFS recommended criteria for freshwater organisms varies with hardness (Thurston et al. 1979):

hardness (mg/l $CaCO_3$)	Total Zn (mg/l)
0 - 75	0.050
75 - 150	0.050
150 - 300	0.10
300 - 400	0.30
> 400	0.60

- concentrations in soil, 90 mg/kg; natural waters, 0.01 to 1.18 mg/l; in sediments, 10 to 3500 mg/kg (EPA 1976, Leland et al. 1978)
- essential trace element for all organisms
- occurs in freshwater as a labile ionic form (Zn^{2+}) and stable inorganic form ($ZnCO_3$); little association with organic colloids (Florence 1977)
- Zn ions may absorb strongly and permanently in silt, becoming inactivated in aquatic systems (Skidmore 1970)
- toxicity to fish and invertebrates influenced by pH, temperature, and hardness of the water; and by biotic variability (species, age, condition) (Thurston et al. 1979)
- acute and chronic effects to aquatic organisms
- bioaccumulated by freshwater organisms (Uthe and Bligh 1971, Vaughan et al. 1975, Phillips and Russo 1978); depuration slow (Jones 1978)
- toxicity lowered (antagonism) by alkaline earth ions, particularly Ca, thus less toxic in hard water (Lloyd 1961, Sprague and Ramsay 1965)
- may combine with Cu and Ni to be more toxic (synergism) (Brown and Dalton 1970, Eaton 1973a).

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